DISTILLATION OF SAWDUST IN A FLUIDIZED BED

II. ANALYSIS AND YIELDS

A THESIS

Presented to

the Faculty of the Division of Graduate Studies

Georgia Institute of Technology

In Partial Fulfillment

of the Requirements for the Degree

Master of Science in Chemical Engineering

by

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June 1951

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Undated

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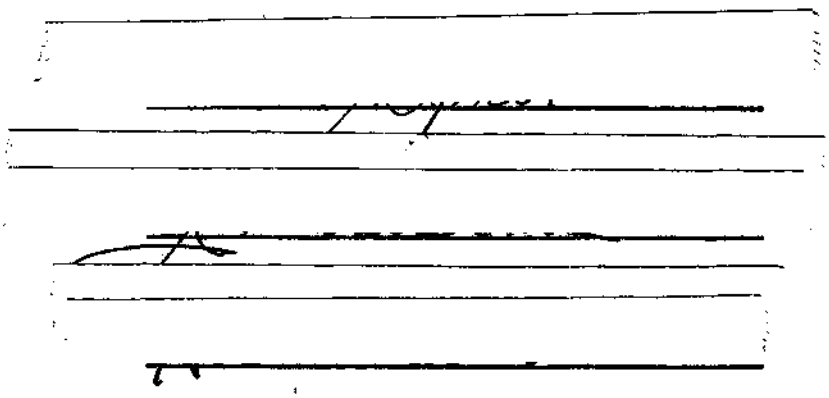

Date Approved by Chairman May 29, 1951

ACKNOWLEDGMENTS

The names and contributions of all the persons who gave generously of their time and effort to help this project toward completion would fill many pages. Of these, my advisor, Dr. H. C. Lewis and my co-worker, Mr. G. M. Armstrong were outstanding. The entire research staff of the Crossett Lumber Company cooperated wholeheartedly in rendering experienced judgment and giving specific information relative to current commercial practices in wood distillation plants and laboratories. Mr. R. H. Byers and his staff at the Georgia State Board of Health gave help far beyond common courtesy. Dr. J. M. Dalle-Valle gave time-consuming assistance in dozens of instances. For patient help during time-consuming analyses and the typing of many revisions, Mrs. Evelyn Garrison Morgan, my wife, deserves especial acknowledgment.

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SUMMARY

Hardwood distillation has been carried out successfully on red oak sawdust, and the process has been evaluated by measuring the yields of a few typical products with time. Interest in this application of fluidization stems from the cheap raw material, greater reaction rates, and isothermal pyrolyzing conditions.

Equipment was designed and constructed to control the reactor temperature closely, achieve the highest degree of fluidization possible on a semi-pilot plant scale, recover all of the products possible, and permit the measurement and analysis of products as functions of time. Liquid product was collected as condensate and mist, and vapor in the fluidizing gas was adsorbed on activated charcoal and recovered by desorption from a vacuum oven into cold traps. Gaseous product was determined by Orsat analyses and flow rate measurements and as desorbate loss from the cold traps. Acid was analyzed by pH curves using pH = 8.3 as an indication of acetic acid content. Methanol was analyzed by liberating equivalent iodine with its nitrous ester derivative.

The Orsat analysis for carbon dioxide was checked by subjecting the outlet gases to a potassium hydroxide scrubbing tower which gave a 20% lower analysis.

It was found that the yields of acid as acetic and methanol were approximately equal to those expected of conventional pyrolysis (8, 16). The rates were so great that 93% of the liquid was produced in 10 minutes and after 30 minutes no more condensate formed. Further studies appear fully warranted.

INTRODUCTION

The dry, destructive distillation of wood for the recovery of charcoal, pyroligneous acid, tar, and gases has been practiced since the days of Ancient Egypt. Up until recently, however, it was enough to produce charcoal alone for use in the iron industry, for which it sufficed to pyrolyze stacks of wood slowly in insufficient air, the reaction being exothermic. Now, however, it is necessary to recover all of the products possible.

The simplest plant which permits the recovery of the tar and pyroligneous acid is built around steel retorts which are charged with wood. The gases and vapors are passed to a water cooled, vertical condenser, the non-condensable gases being used as fuel and the pyroligneous distillate being run off to settling tanks where some tar separates. A more common plant consists of ovens into which buggies of wood are pushed for heating and coolers where the charcoal is denied air until it will no longer burst into flame. The Ford Automobile Company has a vertical retort which permits wood chips to pass downward, being preheated to reaction temperature by hot gases evolved from chips below which have attained sufficient temperature for the pyrolysis to become exothermic. At the bottom charcoal is removed, cooled, sized, and briquetted.

In 1870 the calcium acetate process for the recovery of acetic acid was introduced. Methanol and acetone had already been recovered by distillation to meet the needs of synthetic organic chemistry. In rapid succession since the First World War, acetone, acetic acid, and methanol have been synthesized on a commercial scale and all but smothered the wood distillation industry. However, at the present time the industry seems to have steadied to supply the relatively limited market for charcoal and impure solvents, and by using only scrap wood and applying sound chemical engineering, continues as a source of methanol, acetone, and acetic acid.

In order to strengthen the economics of the hardwood distillation industry, efforts are being made along three lines--cheaper processing, the utilization of sawdust as a raw material, and the recovery of additional or more valuable products.

The processing costs are tied to the small capacity of the ovens (24 hours being a usual cycle), to the 70% of water contained by the pyroligneous liquor, and to its tar-forming constituents which limit the choice of procedures. For example, to eliminate difficulties caused by tar formation, some processes distill all of the water twice.

For years efforts to utilize sawdust have not been

successful because the tars evolved by the sawdust in most intimate contact with the heating surfaces usually serve as a glue for the balance. Another difficulty arises from the structure of wood. By nature, wood has a porous structure with lignin in between the cellulose fibers, and it is from this lignin that the pyroligneous acid and tar come during distillation. The wood itself is an insulating material, and, as distillation proceeds, the pores which form make the charcoal an even better insulator because the gases which fill the pores have such poor conductivity. Thus the transfer of heat to and from wood being distilled requires large temperature gradients which get progressively larger as the process continues. The pyrolysis becomes exothermic when the temperature is high enough, and although variously reported, the critical temperature is believed to be nearly 385° C. for red oak (9) and not much different for other hardwoods. The consequent liberation of large amounts of heat complicates the process because the innermost part of each piece of wood is the last wood to pyrolyze, and it is surrounded by charcoal which confines the heat liberated; consequently, high temperatures result which cannot be controlled. Because of the combination of poor heat conduction and an exothermic reaction, the distillation of wood has always been best carried out in three periods. First, heating is rapid to

distill principally water. Second, outside heating is reduced while the reaction proceeds exothermally. Third, the temperatures are raised to complete the removal of tar. Thus, although small pieces would permit shorter heating cycles, sawdust has never been used commercially.

The possibility of utilizing sawdust has been studied recently at Georgia Institute of Technology and it has been shown that the balling up of sawdust can be avoided by charging it directly into a reactor of the "fluidized bed" type, with the bed having a large heat capacity relative to sawdust and already heated to exothermic temperature (9).

Recently, acetol acetate and maltol have been marketed in an effort to increase the value of wood distillation products and there is hope of adding many other chemicals to the list (11). Pyroligneous acid and its tar are known to contain hundreds of different organic compounds in small amounts. However, as seen above, the temperature history of wood being pyrolyzed by conventional processes cannot be controlled. It is reasonable to expect that only close temperature control would make it possible to alter favorably the kinds and quantity of compounds produced. Therefore, the research program necessary to develop their recovery has been slow because efforts made on one distillate do not necessarily apply

to another. Close temperature control would also improve reproducibility not only from the standpoint of plant operations, but also of laboratory control on the wood charged and the products obtained. The mechanism of hardwood pyrolysis bears out this viewpoint.

Upon preliminary consideration, the fluidized powder technique as a method by which to carry out the pyrolysis of wood seems to offer solutions to a number of the major problems of the wood pyrolysis industry. A few years ago the petroleum industry, in the face of similar problems, set up large scale fluidizing units to catalyze the cracking of petroleum vapors on the surface of finely powdered clay particles. By passing the vapors upward through a bed of clay particles at a gas velocity sufficient to support the bed, it was found that a smooth tumbling motion would ensue if the particles were of a suitable size distribution. Fluidization appeared to be favored by a majority of medium sized particles, some larger particles to act as a filter for them, and enough small particles to "buoy" them up and keep them jiggling. This motion so resembled a boiling liquid that it was called fluidization. Carbon deposited on the clay during the cracking process had to be burned off, and it was necessary not to exceed a certain temperature to keep from ruining the surface of the clay. Again fluidization

was used and temperature differences within the reacting bed were never greater than 10° C. in spite of the large heat of combustion and the poor heat conductivity of the gases and particles of clay. Fluidization, then, brings about reactions between fine particles and gases in such a way that in spite of large heat effects and poor conductivity of the reactants, the reaction is nearly isothermal. The large amount of surface increases reaction rates, and temperatures throughout the bed are more uniform on a large scale than on a small scale.

The greater reaction rates expected for sawdust, as compared to cord wood or chips, would increase plant capacity. Its close temperature control would spur interest in the recovery of more salable products and permit laboratory control and development with a reproducibility heretofore unknown. In addition, there would be the possibility of using the charcoal so formed for new purposes. Inasmuch as the charcoal would already be of the proper size distribution, it could be activated or otherwise reacted by fluidization.

Fluidization, observed visually in this laboratory in glass equipment at room temperature, required rather specific conditions. When the sawdust was ground to a size distribution of 70/200 mesh, and gas was passed upward through about a pound of it in a 2 inch pipe with

a superficial velocity of about 0.7 ft./sec., smooth fluidization ensued. It was also necessary to introduce the gas to the bed by a reasonably good diffuser such as a perforated plate. Fluidization is best detected by small, steadily recurring fluctuations of the pressure drop across the bed, known as jiggling. A sudden drop in bed pressure means that a channel has been formed up through the bed and that fluidization has ceased. Channelling is often caused by the presence of too many fine particles. Large irregular changes in bed pressure mean that slugs of the bed have stopped fluidizing and are alternately being gas-lifted and allowed to fall apart. Slugging indicates that the particles are either too large or too needle-like in shape or perhaps that the reactor is too small or the bed is too heavy.

In order to test the applicability of fluidization to the distillation of sawdust, preliminary work was carried out by Jongedyk (13), and Dimitri (9). In view of the encouraging results of the preliminary work, which showed that sawdust could be pyrolyzed in a fluidized bed, work was planned to investigate the process in greater detail. The previous work had suffered from two handicaps. First, temperature measurements had showed that there were large thermal gradients in the equipment due to large heat losses at the ends. This meant that the

data obtained did not correspond to the truly isothermal conditions which would be expected on a plant scale. Furthermore, considerable tar had been deposited on the piping where it polymerized. In the second place, it was not possible in the early exploratory experiments to obtain reliable mass balances and truly dependable yield data. This was partly due to the difficulty of measuring the noncondensable gas evolved during distillation, which was found to be quite small compared to the fluidizing gas and partly also to the necessity of estimating the amount of solvent vapors swept out of the condenser by the relatively large amount of fluidizing gas. In addition, the literature indicated that considerable mist is usually formed which is not removed in a simple condenser.

Two programs were outlined, one to attain more nearly isothermal fluidization and a mass balance, and another to take yield data and analyze it for the rate of production of pyroligneous acid, gas, and four typical compounds--methanol, acid as acetic, carbon dioxide, and carbon monoxide. The two programs were coordinated to take data on the same runs. The first program will be reported by G. M. Armstrong, Jr. (4) while the measurement and analysis of the yields will be dealt with fully in this paper.

APPARATUS AND EXPERIMENTAL PROGRAM

A block diagram of the reactor and recovery train employed in the experimental work is presented in Figure 12. The details of the reactor and water-cooled condenser, as well as the preparation of the charge, will be discussed by Armstrong (4). The following section deals with the recovery system following the water-cooled condenser.

1. Measurement of Liquid Product

Previous calculations of pyroligneous liquor loss with the outlet gases (9) was based on the assumption that the vapor pressures of the components in pyroligneous liquor obey Raoult's law. The large amount of nitrogen necessary to bring about fluidization, together with the non-condensable gas evolved from wood pyrolysis, carried out a considerable quantity of vapor, according to the calculations, and significantly higher yields of acetic acid and methanol were predicted than are obtained commercially. An actual recovery of this vapor was therefore desired and two methods were proposed, the first to add one or more low temperature condensers, the other to employ adsorption on charcoal. Both involved complications, but the availability of a vacuum oven large enough to desorb the quantities of charcoal needed caused the charcoal adsorption method to be chosen.

Preliminary work on small scale apparatus indicated that commercial activated charcoal was suitable and that losses would be negligible. Cans were constructed of 14 gauge sheet iron 10 in. high with 6 in. diameters to contain 2000 g. of charcoal and weigh about 3500 g. complete with adsorbent and suitable fittings. Full scale experiments were conducted at expected gas flow and the results

were satisfactory (3). Vapor pickup could be weighed to within 0.5 g. and repeated adsorption and desorption gave a constant desorbed charcoal weight to within a gram. Desorption was standardized to use a temperature of 140° C. and 4 mm. Hg. absolute pressure. A dry ice and methyl-ethyl ketone trap was used followed by a liquid nitrogen trap. As shown in Figure 12, three adsorption cans were used during a run--two in parallel to permit weight with time measurements and a third to serve as clean-up. The cans in parallel were fitted to facilitate removal for rapid weighing.

The recovery of the pyroligneous acid which would condense in the water-cooled condenser offered no problem except that of mist. Tarry mist conveyed to the activated charcoal would most likely deactivate it and not be removed by the desorption process. Indeed, its nature is to polymerize when either heated or stripped of its volatile components. Therefore, a mist cup was designed to trap most of the mist and this was followed by a glass wool plug. The condensate was received in a separatory funnel and increments removed at intervals into tared test tubes. The recovery train added to the water-cooled condenser, then, consisted of a mist trap, cans of activated charcoal, a gas sampling manifold, a rotameter and, during one run, a carbon dioxide scrubber. In order to

simplify the discussion, the condensate and mist taken together will be called the "liquid" while the sum of the liquid and the vapor will be spoken of as the "total liquid."

2. Measurement of Outlet Gas Flow and Composition

Previous work on the pyrolysis of fluidized sawdust (9) had indicated that the flow of outlet gas (that is, the fluidizing gas plus the gas evolved from the charcoal) varied by a factor of two, and its composition with respect to carbon monoxide, carbon dioxide, and methane varied a hundred fold, both variations taking place within minutes. It was not clear whether the rapid variations in outlet gas were caused solely by corresponding variations in gas evolution or perhaps partly also by acoustical effects. These latter would result (in analogy with electrical phenomena) from sudden impulses of flow or pressure (current or voltage) within a network of spaces (capacitors), orifices (resistors), and moving masses (inductors) in the fluidized bed. This uncertainty ruled out the relating of instantaneous flow with the rate of gas evolution from the sawdust at exactly the same instant, but it was thought that delays of response would be less than a minute. In any event, the flow at any one point was determined by a rotameter and from

readings taken at sufficiently short intervals, curves were drawn of flow versus time. A reliable single measurement of inlet nitrogen was made by a simple orifice, because the flow was made critical through the needle valve on the pressure regulator. Then, having established the equipment leak by blank runs, the outlet flow of nitrogen was calculated and the total evolved gas calculated by difference. Gas samples were taken from the gas stream immediately preceding the outlet flow rotameter so it could be argued that a sample taken at a certain time represented the composition of the flow indicated by the rotameter at the same time.

A manifold with twelve inverted 250 cc. Erlenmeyer flasks was built to permit the taking of gas samples by simply opening and closing a stopcock. Acidulated sodium sulfate solution was chosen as confining fluid because mercury would have been too heavy and too dangerous. A standard Orsat analyzer was obtained for the analyses of the gas samples. Carbon dioxide was analyzed by absorption by acid cuprous chloride. Methane was analyzed by slow combustion. Hydrogen was not expected at the temperature level employed, but the slow combustion method permitted simultaneous analyses for carbon monoxide, methane, and hydrogen. The idea of collecting the total gas in a gas holder was attractive from the analysis standpoint but

was never seriously considered principally because previous runs had indicated that the holder would have to be quite large. Runs of 120 min. had been used (9) indicating 72 ft.^{3} of fluidizing nitrogen alone. It was therefore decided to use the simpler technique.

Because of variations in flow and composition, it was felt that reliable yields could be proved only by making a direct measurement of the total amount of each major constituent evolved. Thus, total carbon dioxide was scrubbed out by a strong potassium hydroxide solution in an efficient absorption tower. Oxidation of carbon monoxide to carbon dioxide, followed by absorption in a second scrubber, was considered. Methane cannot be chemically analyzed with any simple technique but was expected to be low at the temperature level of the runs.

Preliminary testing on the carbon dioxide scrubber indicated that a suitable absorbent was a 40% KOH solution, technical grade, and the scrubber should be packed with about 20 in. of packing in order to reduce the carbon dioxide concentration to about 0.1%. A bubbler with sixteen small holes about 1 mm. in diameter was found to distribute the gases through the absorbent so well that a gas-lift recirculator for the caustic was unnecessary. At the bottom of the scrubber a stopcock was fitted to

permit the taking of samples of the caustic with time. Figure 13 contains a scale drawing of the scrubber. The standard double end point titration for carbon dioxide was adopted using a Beckman pH meter. In order to protect the glass electrode, the solution was titrated to an alizarin blue end point before using the electrode. In order to protect the outlet rotameter from possible spray from the scrubber, the absorber was added to the recovery train following the outlet flow rotameter. The pressure drop through the scrubber necessitated, then, a density correction for the rotameter calibration for any run during which the scrubber was used.

Experiments conducted on the oxidation of carbon monoxide by a high temperature bed of copper oxide proved that the oxidation is rapid and complete just so long as half of the bed is fresh copper metal. In the equipment built there was sufficient capacity for both the copper and enough of its oxide to convert the 6% of carbon monoxide expected on the basis of wood charged. However, since the reliability of the gas analysis by the sampling technique was proved by analyzing for carbon dioxide by both methods and getting a check, the oxidation of total carbon monoxide was not used.

The principle involved in measuring inlet nitrogen (namely, that flow through a critical orifice is indepen-

dent of downstream properties and is perfectly constant for constant upstream gas density and temperature) suggested another technique for continuous gas analysis (18). One or more side streams from an outlet manifold (therefore at atmospheric pressure for all gas rates) could be directed through a critical orifice, an analysis train, and a properly trapped water aspirator. Small flows known to be exactly constant would result just as long as the ratio of upstream pressure to downstream pressure across the critical orifice was at least 0.53. The flexibility of this method was intriguing but it was discovered that extremely small orifices would be required and development time was lacking. With small flows a much better analysis for carbon monoxide could be used, namely, the reduction of iodine pentoxide to iodine at a temperature of 140° C. held constant by a dibutyl ether vapor bath. Methane could be absorbed at a low temperature in a liquid hydrocarbon where it could be detected by refractive index. As a last resort a slow-combustion train with added oxygen could be utilized to analyze for methane.

3. Chemical Analysis

A rapid method for the chemical analysis for acetic acid was not found. However, it was assumed that a variation of the industrial procedure of titration to pH = 8.3

would give a reliable measure of acetic acid. It was felt that since commercially over 90% of the acid found is acetic and since under isothermal conditions less polymerization would be expected, a pH curve would suffice.

The methanol analysis customarily made on pyroligneous liquor is typical of empirical industrial control and is unsuited to the evaluation of product obtained under conditions thought to be more favorable to methanol production. A survey of the literature indicated that a chemical analysis for methanol exists which is specific, excepting for possible interference by allyl alcohol which is usually present in very small amount in pyroligneous acid. The nitrous acid ester of methanol, which is extremely volatile, is passed through potassium iodide solution where it quantitatively releases equivalent iodine (10). Cylinder nitrogen, used as the inert gas to sweep the ester through the bubblers, was regulated by a reducing valve and a manometer to a flow of 7 l./hr. The five bubblers served the following purposes:

No. 1 took out oxygen with pyrogallol.

No. 2 was the reaction chamber where the nitrite was formed.

No. 3 removed the oxides of nitrogen with caustic.

No. 4 reduced the nitrite with potassium iodide.

No. 5 reduced last traces of nitrite with potassium iodide.

All the bubblers except No. 2 were standard fritted glass gas washing bottles with a capacity of about 200 ml. Bubbler No. 2 was a vessel made from 35 mm. glass tubing provided with a bubbler, a gas outlet to the other bubblers, and a dropping funnel with a connection to upstream nitrogen to balance the pressure inside the reaction chamber. A by-pass around the reaction chamber permitted the reaction chamber to be changed without interrupting the sweeping. A methanol vapor bath was placed around the reaction chamber in order to make all runs at about the same temperature, namely 65° C. It is drawn to scale in Figure 13.

4. Distillation Analyses

As a check on the chemical analyses, and to further characterize the nature of the products, separate true boiling distillations were planned for the vapor and liquid. Since only the more volatile substances would get through the condenser and mist trap to the charcoal, the vapor would probably be easy to fractionate by distillation. Fractionation of the liquid would be less satisfactory because of the large amount of water expected. Therefore, an efficient fractionating column was constructed with separate reflux and product condensers (see Figure 13). The product condenser was designed to be shut off

automatically as soon as the overhead vapor exceeded any predetermined temperature. Thus the fraction of the liquid with the boiling point range in between any two temperatures could be easily determined with only two limitations. The first was the amount of vapor which would condense while the product condenser was being shut off, and the second was the amount of distillate above the packing as vapor or as liquid on the walls of the condenser. The holdup on the packing would of course affect the degree of separation between two successive fractions but would not limit the amount of material in any one fraction.

The column was to be used to remove the compounds with boiling points below water. Then, following plant practice, ethyl acetate would be used to extract the acids, oils, and tars from the water. Three extractions using equal volumes of solvent and liquid are reported (8) to remove 98% of the acetic acid. Separating the volatile acetate by fractional distillation from the extract would leave the acids, oils, and tars practically water free. It was planned to fractionate the acetic acid from the oils at an absolute pressure of 4 mm. Hg. to minimize polymerization of tars in the still pot. Since the fractionating column had a holdup of about 30 ml. and the liquid was expected to contain only 12% acetic acid,

700 ml. would be the minimum amount of liquid to begin with. Since about 150 ml. of liquid was expected per pound of sawdust, the combined liquid from five runs would be necessary. The total vapor for the same runs was to be allowed to accumulate in the adsorption cans to be desorbed all together.

A test on the efficiency of this column by Bauer (6) and Armstrong (2) indicated that at infinite reflux and a boilup rate of about 30 ml./min. a CCl_4 - C_6H_6 mixture separated to the extent of about twenty theoretical plates.

PROCEDURE

Four pyrolysis runs were made to permit qualitative observations of leaks and unexpected conditions. Since sudden drops of pressure on the manometer across the fluidized bed indicated channeling, a perforated plate diffuser for the fluidizing gas was constructed to insure fluidization. Leaks were reduced to a minimum, and a good check on inlet and outlet nitrogen was secured. The sawdust charging device originally planned had to be replaced. The addition of electrical heater windings to prevent heat losses had so increased the temperature of the original charging chamber that the sawdust distilled partially as soon as it was added to the charger. The new charging device was filled with sawdust before it was fixed to the column, and the sawdust was blown directly into the reactor bed before the charger had been heated. Time was measured from the instant pressure appeared on the manometer across the reactor bed. Condensate was observed to form a great deal faster than had been expected from previous work, and ceased to form altogether after thirty minutes. The decrease in run time from two hours to thirty minutes was attributed to the improvement in fluidization resulting from the better diffuser. After the perforated plate was put into use, the bed manometer

pressure jiggled regularly and its average fell slowly during pyrolysis in accordance with the decrease in bed weight.

Five successive runs were then carried out on August 10, 1950 under as nearly identical conditions as possible. Since the first of these (Run 5) was carried out at 411° C. inadvertantly, effort was made to carry out the other four runs also at 411° C. However, the temperature of the reactor was found to be too sensitive to small changes in the settings of the variacs. Large heat losses, in analogy with the flywheel effect in mechanics, had made the column relatively insensitive to small changes of heat input during the early work. The elimination of much of the heat loss by added insulation and guard windings had removed the flywheel to a large extent. As good a mass balance as possible was obtained for all five runs, but, because of the complications involved in securing rate data, the kind of rate measurements made was changed from run to run. For example, gas analysis data were obtained only for Run 7. Product charcoal, condensate, mist, and sorbate on the other hand were measured for all runs because the measurements were easily made after each run. Product charcoal recovery proved to be an unexpected problem, and when it

could not be recovered at the end of a run, it was removed by blowing compressed air up the hot reactor until no more explosions occurred. Condensate gave no problem at all. It was simply collected and weighed. Tar, as such, did not appear in the original liquid. Only a third of the mist passed through the mist cup and deposited on the glass wool and its container. Charcoal adsorbate was weighed by removing the adsorber cans from the train and weighing them on a triple beam balance. For Runs 5 and 9 only the above measurements were made.

For Runs 6 and 8, emphasis was put on total liquid rate. Condensate was removed from its receiver into tared test tubes at intervals to permit the plotting of a curve of liquid yield vs. time. The mist could only be measured at the end of the run, but it was assumed to have been produced at the same rate as the condensate. Sorbate production was measured with time by weighing one can while another can was adsorbing. The clean-up can never did pick up any sorbate. The adsorbate was pumped from the charcoal at a pressure of 4 mm. Hg. and a temperature of 140° C. and the desorbate was collected in two traps. The first was cooled with dry ice and methyl ethyl ketone, and the second was cooled with liquid nitrogen. After desorption, the traps were removed from their refrigerants and brought to room temperature. Then

the recovered adsorbent was collected and weighed as vapor. The rate of production of vapor was assumed to have been proportional to the rate of pickup of adsorbate on the charcoal, thus distributing the recovery loss proportionately. Inlet nitrogen was measured by the pressure drop across a calibrated orifice, and outlet nitrogen before and after the runs was measured by a calibrated rotameter.

For Run 7, the absorber was added to the recovery train just following the outlet rotameter. 40% potassium hydroxide was poured into the scrubber and two cyclone traps were added to the gas outlet to recover and return entrained caustic. The gas sample bottles were filled with confining fluid, and during the run twelve gas samples of over 200 ml. each were taken for Orsat analysis. A minimum of confining liquid, about 1 ml., was left in the sample bottles when the sample was taken, about 0.5 min. being required to displace the confining fluid with gas during sampling. The outlet rotameter was read at intervals of about thirty seconds. One caustic sample was taken before the run and six were taken during the run.

Following Runs 5 through 9, the vapor was recovered from the charcoal and analyses were made. For Runs 6 and 8 two aliquots were taken from each increment of condensate, and acid as acetic and methanol analyses were made for

each increment using a pH titration curve for the acid, and a special analysis (10, 19) for the methanol. The vapor recovered from all five runs was likewise analyzed for acid as acetic and methanol. Aliquots were taken from the caustic samples and a pH curve was obtained for each one.

The methanol content of pyroligneous acid was analyzed by allowing the methanol to react with nitrous acid. The nitrite of methanol so formed is very volatile (B. P. = -12° C.), insoluble in water, and will liberate iodine quantitatively from acidic potassium iodide. The iodine was titrated with twentieth normal sodium thiosulfate.

The following procedure was used in all runs.

100 ml. of 50 wt.% KOH was added to bubbler No. 1, then 5 g. of pyrogallic acid dissolved in 10 ml. of water was added. The flow of nitrogen was adjusted to a rate of 7 l./hr., which was maintained throughout the subsequent procedure. Bubbler No. 1 was placed in the train and swept out with nitrogen.

25 g. of anhydrous $NaNO_2$ and 30 ml. of distilled water were placed in a 50 ml. Erlenmeyer flask. The Erlenmeyer flask was stoppered and shaken keeping air out as much as possible. 25 ml. of this solution was placed into the esterifying chamber which was then placed

in the train. The methanol vapor bath was then begun and nitrogen was bubbled through the separatory funnel and reaction chamber.

100 ml. of 15 wt.% KOH was added to bubbler No. 3; it was then placed in the train and swept with nitrogen.

4 g. of KI and 60 ml. of 0.5 N HCl were added to bubbler No. 4; it was then placed in the train and swept with nitrogen.

2 g. of KI and 60 ml. of distilled water were added to bubbler No. 5 together with ten drops of concentrated HCl (sp. gr. 1.18). Then bubbler No. 5 was placed on stream.

The whole train was run for ten minutes. In the meantime, 13 ml. of glacial acetic acid was mixed with the sample to be tested containing not more than 100 mg. of methanol. This was placed in the separatory funnel and added to the reaction chamber dropwise.

Preliminary testing showed that 1.00 milliequivalent of thiosulfate was used per millimol of methanol charged, to within 1%. Acetone does not interfere. Although ethyl alcohol, allyl alcohol, and methyl acetate will interfere no correction was attempted for the following reasons. Ethyl alcohol is not reported as a product of wood pyrolysis. Although allyl alcohol interferes, it is present in small amount compared to the methanol,

and after being separated from the tars and oils can be determined by bromine. Methyl acetate was tested and iodine was liberated equivalent to the hydrolysis of 16%. However, the presence of 8% methanol as an impurity would have given the same results and this latter interpretation is favored for two reasons. First, acetic acid is a weak acid. Second, the iodine which was liberated formed quickly and there was no noticeable deepening of the color with time. Ordinarily hydrolysis is a slow reaction which continues as long as one product is removed. Methanol-free methyl acetate was never tested.

RESULTS

The overall yields obtained from pyrolysis of red oak sawdust at an average temperature of 406° C. are presented in Table XI.

Cumulative yields as a function of time are summarized in Figures 1 - 6 and 10. The data on total liquid yields are presented in Figures 1 and 2, the data on acetic acid and methanol in Figures 3 - 6, and the data on evolution of carbon dioxide, carbon monoxide, and other gases (presumably chiefly methane) in Figure 10.

The instantaneous rates of production are shown as a function of reaction time in Figures 7 - 9 (gas rates) and 11 (total liquid, acetic acid, and methanol).

For the original data, methods of calculation, and calculated values on which the above tables and figures are based, reference should be made to the tables in the Appendices.

DISCUSSION OF RESULTS

1. Overall Yields

The order of reproducibility during these runs is indicated by Table XI. Since all yields are presented on a basis of 100 g. of dry sawdust, the weight of the net charge will exceed 100 g. by the amount of free moisture it contains.

Comparison of these overall results with those obtained by Dimitri (9) is best made on the yields of charcoal and condensate, and the percentage of acid as acetic and of methanol found in the condensate. His run made at 385° C. most nearly corresponds to the runs reported here. He recovered 32.0% charcoal compared to 31.6% recovered during Run 7. The lower yields of charcoal on Runs 6 and 8 resulted from the sticking of charcoal to the reactor. This charcoal was burned out between runs by blowing jets of compressed air up the reactor until explosions ceased. On charcoal, then, there is excellent agreement. Dimitri reported the yield of tar plus distillate as 21.9% which is significantly lower than the 27.7% and 28.2% condensate reported here for Runs 6 and 8 respectively. However, he observed that liquid product was continuing to form at the end of the run. Thus the increased yield reported here is attributed to the more

complete distillation which resulted from the improved inlet gas diffuser. It should be noted that in addition to the increase in condensate recovery which was obtained by the same water condenser Dimitri used, considerable mist was recovered. The mist and condensate combined make up the liquid product as defined in this report.

Dimitri used a phenolphthalein end point as a measure of acetic acid whereas in this work pH = 8.3, read from a pH-titration curve, was used. Dimitri obtained an average weight percent of 19.4% acid as acetic in his condensate which compares favorably with the 18.4% and 17.8% obtained for Runs 6 and 8 in this work. Methanol as determined by the Othmer method (17) gave a higher yield than was obtained by the Fischer and Schmidt method (10). Thus Dimitri reported a methanol analysis of 5.1% for his condensate as compared with the 3.17% and 3.27% methanol obtained for Runs 6 and 8 in this work. Since the Othmer analysis includes as methanol any acetone and methyl acetate present, his results were expected to be high (9).

Yields of acetic and methanol reported in the literature are difficult to interpret because the ordinary distillation process itself is, by nature, difficult to reproduce, and, furthermore, the customary methods of analysis in the plant are empirical. Several acids, principally

propionic, formic, and butyric, contribute to any titration analysis for acetic acid, and the term "crude methanol," used often in the wood distillation trade, includes acetone, methyl acetate, and some water. Even the same specie of wood grown in different regions has been reported (12) to give large variations in yields. Because there are so many unknown sources of variation, comparison of the fluidized distillation yields with an average of the yields obtained by customary destructive distillation would not evaluate the process. It was thought that two comparisons, one with yields reported for good commercial operation on mixed oak, and one for laboratory yields on steam distilled red oak would be more significant. For acid as acetic, the average of Runs 6 and 8 was 5.85% compared with 3.1% for commercial practice (8) and 5.37% for laboratory steam distilled red oak (16). For methanol, the average of Runs 6 and 8 was 1.05% compared with 1.0% for commercial practice (8) and 2.25% for laboratory steam distilled red oak (16). However, this last figure is thought to refer to "crude methanol" which would represent about 1.0% pure methanol.

These comparisons show that the fluidized powder technique of distilling sawdust gives results which compare favorably with both plant and laboratory distillations carried out using chips or sticks. The reproducibility

of the yields of both acetic acid and methanol was ± 0.05% of the weight of the charge. Large scale fluidizing equipment would give even better reproducibility. Also, the use of a simple, specific test for methanol using common reagents and equipment has been proven successful, and further application of it would make reported yields of methanol more significant.

2. Cumulative Yields of Total Liquid, Acid as Acetic, and Methanol

The most noteworthy point about the data on yields as a function of time is the relatively short reaction times required for substantial completion of the distillation process. Thus Figures 1 and 2 indicate that reaction is practically complete after 30 minutes. Visual observation on longer runs indicated that no more condensate at all forms after 30 minutes. This compares with times on the order of 2 hours reported by Dimitri (9) and 24 hours in present commercial practice. Dimitri's reaction was presumably slow because there was no adequate diffuser for the inlet gas.

The exact significance of the yields requires some explanation of the methods of calculation. Total liquid was defined to correspond to the significance of those words when used in conventional pyrolysis. In order to take into account the differences, it was necessary to

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consider the material adsorbed on the charcoal to consist of two parts: liquid material which would have been condensed in the water condenser in the absence of large volumes of fluidizing gases, and gaseous material which would ordinarily not be subjected to activated charcoal. The former is called vapor in the normal sense of the word, but the latter is simply called adsorbate gas.

Referring to Table VIII it will be noted that only 52.7% of the combined adsorbate for Runs 5, 6, 7, 8, and 9 was recovered. The adsorbate pickup for previous runs corresponded to within 1 g. of the loss in weight of the adsorption cans plus adsorbent, and it is therefore inferred that nearly all of the material adsorbed was actually desorbed under the treatment of 150° C. and vacuum of 4 mm. Hg. With the exception of hydrogen and carbon monoxide, liquid nitrogen will quantitatively condense or crystallize all of the normal compounds of wood pyrolysis if the pumping down is conducted slowly enough to cool the desorbate. A pinch clamp in the suction tubing just following the liquid nitrogen trap was adjusted to keep the absolute pressure on the vacuum pump about 10 mm. Hg. When the desorption was almost complete, the pressure fell to 4 mm. Hg., the limiting pressure of the pump. An hour later the desorption was considered complete. Therefore, there was little or no loss of desorbate during

desorption from the two cold traps. The 47.3% of the adsorbate which was lost from the cold traps was the material which boiled and sublimed from them on warming and is mentioned in Table VIII. The analysis of this lost material would have required the use of a gas holder sufficiently large to contain their gaseous volume or a flow sampling technique such as that used on the outlet pyrolysis gas. It was decided to omit the analysis of gaseous adsorbate inasmuch as its weight was known. Further refinements of this nature would have deferred the results of the project without clearing up the immediate problem of determining the yields and rates.

The percentage of the total adsorbate for Runs 5, 6, 7, 8, and 9 which was proved to have been vapor, 52.7%, was assumed to apply for each run separately and for the incremental yields during each run as well. The vapor yield points in Figures 1 and 2 are, then, simply the adsorbate yield points multiplied by the average ratio of vapor to adsorbate. The yield of mist with time was assumed to be proportional to the yield of condensate with time. Therefore, the yield points of liquid in Figures 1 and 2 are condensate yield points adjusted by simple proportion to include the corresponding mist. Inasmuch as the yield points for condensate and for vapor could not readily be taken at exactly the same

times, the addition of the two yield curves had to be done graphically in order to derive the yield of total liquid with time.

Individual liquid increments were analyzed for both acid as acetic and methanol and their yield time curves, shown in Figures 3, 4, 5, and 6 were constructed in complete analogy with the liquid-time curves in Figures 1 and 2. The acid and methanol yield curves for the vapor had to be approximated in the same way as the vapor yield curves were in Figures 1 and 2. It was of course impossible to analyze chemically individual vapor increments for acid and methanol. The recovered adsorbate for Runs 5, 6, 7, 8, and 9 was analyzed and this average analysis was assumed to have been constant for each run and increment.

It should be noted in Tables III and IV that the analysis of acid shows a pronounced maximum concentration for both runs in which it was measured at about a time equal to 2 min. Methanol, on the other hand, shows a constant increase in concentration right up to the cessation of production.

Comparison of the yields of total liquid with time for Runs 6 and 8 illustrates the reproducibility of liquid yields (Figures 1 and 2). The smoothness of the curves should not be interpreted as an indication of smoothly

changing rate such as is illustrated in Figure 11. Yield curves represent integrations of the rates with time and regardless of the amplitude and frequency of fluctuations of the actual rate, will always be a smooth curve. The graphical derivative in Figure 11 is a result of two graphical averaging processes and represents what would be expected of a large batch reactor operating with negligible transient rate fluctuations.

It will be noticed that each rate-time curve on Figure 11 consists of straight lines on log-log plots with breaks at a reaction time of about 2 min. Curves might be drawn through the data points and indeed if the initial time of heating the bed, about 0.5 min., be charged against the first increment, the rate-time points fit into parabolas on log-log paper. Hence, whether the break in the curves as shown corresponds to a real charge in reaction mechanism or not is not clear. However, an actual "break" is not inconceivable. For example, such a break would occur if the lignin in the wood decomposes quite rapidly at first, controlling the reaction in the early stages, and then disappears almost completely, allowing the decomposition of cellulose to dominate the reaction in its later stages. Another possible factor is an increase in thermal decomposition resulting from the increased residence time of

the gases within the pores of the charcoal as the rate of gas evolution drops off.

The analyses by distillation were not advanced beyond the exploratory stage. The vapor analyzed about 14% crude methanol (crude methanol consists of three binary azeotropes of acetone, methanol, and methyl acetate, and possibly a ternary azeotrope as well). The liquid distillation was ruined by an accident just before acetic acid appeared in the stillhead vapor, but its odor was noticeable. The bottoms proceeded to become a tough, pasty tar after six months.

3. Total Outlet Gas and Evolved Gas

The outlet gas rate data of Run 7 indicate that the acoustical effects predicted do indeed cause variations in instantaneous gas flow. The effect is illustrated by the regular fluctuations in the curve of Figure 8 from 22 min. to 26 min. However, the more pronounced variations, beginning with the large drop in flow rate during the first 2 min. of the run and continuing for about 16 min., are a whole order of magnitude greater than the acoustical effects and are caused by fluctuations in the fluidized bed. Physical fluctuations of the sawdust particles, such as agglomeration followed by explosions, would introduce uneven heat transfer and hence gas fluctuations as more or less material was vaporized in

the pores of the wood. An averaged curve was drawn in order to indicate the gas rate to be expected in a large reactor. The scale used in Figure 7 indicates the accuracy of the gas rate measurements, but in order to aid interpretation, it was assumed that all outlet gas in excess of the outlet rate of nitrogen (0.195 g. mol/min. based on 100 g. dry sawdust) was gas evolved from the sawdust. Two evolved gas rate curves were drawn in Figure 8, one to assist in predicting the averaged outlet flow rate needed for Figure 7, and the other, a curve smoothed through the data points, to aid in locating the instantaneous gas rate immediately following the gas sampling manifold. This latter was the better curve to use for estimating carbon dioxide and monoxide yields from Orsat analysis of samples.

The pyrolysis of the first 2 min. was accompanied by very large flow variations. Initial time was taken as the instant a pressure drop appeared across the bed of the reactor. Immediately there was a drop in outlet gas flow, but the actual rotameter reading varied too quickly to be read. Rotameter plummets need a second or so to reach equilibrium and for the first two minutes the plummet never stopped long enough to be read. A motion picture would have been necessary to have gotten any readings at all during the first two minutes. It

was observed that the outlet gas flow varied from the inlet flow of nitrogen by as much as 50% smaller to as much as 100% larger. The 7.2% free moisture and other quickly vaporized materials which were almost wholly condensed in the water condenser explain, at least in part, the decrease. The time variation of the acoustical effects in this system were about 1 min. per cycle. Therefore, during the initial dropping of the charge and initial flashing of steam, the gas rate does not have opportunity to equilibrate. That some gas was evolved from the sawdust during the first 4 min. is shown by the curve in Figure 10 which contains a plot of carbon dioxide yield vs. time as analyzed by absorption in potassium hydroxide. However, the carbon dioxide coming off so quickly was probably gas which was desorbed rather than chemically produced.

The gas analysis for carbon dioxide by the two methods shows the value of checking results. For example, the indication is that the absorber was only 81% efficient as Orsat analysis in predicting gas yields. Remembering that the formation of a gas bubble is regarded to be attended by more absorption than subsequent scrubbing by packing, especially when gas concentrations are low, it is concluded that two bubblers would result in greater efficiency and one should be added to the scrubbing tower to help remove residual carbon dioxide from the exit gas.

The two peaks in the carbon dioxide evolution rate curve in Figure 9 are believed to represent Run 7 correctly, but in large scale apparatus these two peaks would probably average out to a single peak.

The carbon monoxide rate curve in Figure 9 indicates more emphatically the fluctuations which Run 7 gave. It is not unreasonable to consider two carbon monoxide rate maxima, one for the rapid decomposition of formic acid early in the run, another to represent a more gradual process of decomposition. The presence of much water vapor would repress the decomposition of formic acid during the first two minutes and indeed the pyroligneous acid collected smelled very strongly of this compound and little carbon monoxide was noted until after the rate-time curves on Figure 11 changed slope.

The curves in Figure 9 show that practically no carbon dioxide is produced until after the carbon monoxide production has almost ceased. It would appear that processes which occurred during the first 5 min. of the pyrolysis, e. g. vaporization of water, kept the temperature of the individual sawdust particles below the temperatures at which cellulose decomposes. Thus the bed temperature may have been only of surface depth for the first 5 min.

CONCLUSIONS

1. Yields of acid as acetic and of methanol are (5.85 ± 0.5)% and (1.05 ± 0.05)% respectively, based on oven dried red oak, pyrolyzed at about 406° C.
2. Pyrolysis is completed in approximately 30 min. as attested by the cessation of condensate formation (gases continued to be evolved in small amount).
3. Isothermal pyrolysis of 70/200 mesh red oak sawdust in a fluidized bed occurs in two different ways, one of 2 min. duration and the other becoming two orders of magnitude smaller within 8 min., perhaps involving diffusion as an additional process.
4. Carbon dioxide is not produced in the fluidized bed pyrolysis until carbon monoxide production rate has dropped to 10% of its peak rate.
5. Methanol can be analyzed quantitatively in pyroligneous acid by esterifying it to methyl nitrite and oxidizing equivalent iodide to iodine.

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APPENDICES

APPENDIX A

TABLE I+

Liquid and Vapor Yield Data on Run 6

442 g. charge 7.2% moisture (wet basis)

Temperature of Fluidized Bed
Thermocouple No. 3 Top of Bed 400-405° C.
Thermocouple No. 4 Bottom of Bed 390-392° C.

Cond. Spl. No.	Time (min.)	Cond. Δ Time (min.)	Sorb. Δ Time (min.)	Cond. Δ Wt. (g.)	Cond. Σ Wt. (g.)	Sorb. Δ Wt. (g.)	Sorb. Σ Wt. (g.)
6	0.50	0.50		4.16	4.16		
5	1.00	0.50	1.00	32.36	36.53	7	7
4	2.00	1.00		27.30	63.83		
	3.34		2.34			14	21
3	4.00	2.00		29.02	92.85		
	7.50		4.16			5	26
2	10.00	6.00		15.48	108.33		
	13.33		5.83			4	30
1	30.00	20.00	16.67	5.41	113.74	6	36
		Mist 19.5 g.			Vapor Cleanup 0.0 g.		

+ For the meaning of symbols and abbreviations refer to Appendix B.

TABLE II

Liquid and Vapor Yield Data on Run 8

447 g. charge 7.2% moisture (wet basis)

Temperature of Fluidized Bed
Thermocouple No. 3 Top of Bed 412-415° C.
Thermocouple No. 4 Bottom of Bed 415-417° C.

Cond. Spl. No.	Time (min.)	Cond. Δ Time (min.)	Sorb. Δ Time (min.)	Cond. Δ Wt. (g.)	Cond. Σ Wt. (g.)	Sorb. Δ Wt. (g.)	Sorb. Σ Wt. (g.)
19	1.00	1.00	1.00	28.88	28.88	6	6
8	2.00	1.00		37.40	66.28		
9	3.00	1.00		18.18	84.46		
	3.33		2.33			11	17
10	5.17	2.17		14.18	98.64		
	6.67		3.34			2	19
11	10.82	5.65		11.66	110.30		
	16.18		9.51			(-3)[1]	
12	30.00	19.18	13.82	6.58	116.88	6	25

Mist 20.0 g. Vapor cleanup 0.0 g.

[1] This increment was not included in the running sum.

TABLE III

Liquid Analysis Data on Run 6

Spl. No.	Ali. (g.)	Acid (pT=8.3) (meq.)	Acid (wt. % Acetic)	MeOH Ali. (g.)	MeOH (meq.)	MeOH (wt.%)
6	1.116	2.65	14.3	1.158	1.081	3.00
5	1.146	3.52	18.4	1.224	1.027	2.68
4	1.215	3.65	25.4	1.208	1.237	3.28
3	2.190	3.02	15.2	1.223	1.230	3.22
2	1.140	2.63	13.8	1.106	1.295	3.75
1	0.605	1.51	15.0	0.542	0.614	3.62

wt. of sorbate = 36.0g.
wt. of vapors = 52.7% of 36.0 = 19.0 g. (see Table VIII)

52.7% of the total sorbate from Runs 5, 6, 7, 8, and 9 was recovered, and the mixture analyzed 1.61 wt.% (pT = 8.3) as acetic and 8.28 wt.% MeOH.

TABLE IV

Liquid Analysis Data on Run 8

Spl. No.	Ali. (g.)	Acid (pT=8.3) (meq.)	Acid (wt.% Acetic)	MeOH Ali. (g.)	MeOH (meq.)	MeOH (wt.%)
19	0.962	2.89	18.0	1.095	0.900	2.63
8	1.035	3.26	18.9			2.73[1]
9	1.013	3.10	18.3	1.028	0.946	2.94
10	1.130	3.16	16.7	1.012	1.027	3.24
11	1.138	2.88	15.2	0.918	1.430	4.98
12	1.062	2.61	14.7	0.704	1.515	6.89

wt. of sorbate = 23.0 g.
wt. of vapors = 52.7% of 23.0 = 12.1 g.

52.7% of the total sorbate from Runs 5, 6, 7, 8, and 9 was recovered, and the mixture analyzed 1.61 wt.% acid (pT = 8.3) as acetic and 8.28 wt.% MeOH.

[1] Estimated by interpolation.

TABLE V

Gas Analysis Data vs. Time on Run 2

Time (min.)	Rot. Rdg. (mm.)	Uncorrected C.F.M.	Spl. No.	% CO_2	% CO + % CH_4
0.0	60	0.54			
0.5	60	0.54			
1.0	60	0.54	1	0.0	4.4
2.0	63	0.59	2	0.8	5.8
3.0			3	0.8	
5.0			4	1.6	1.6
7.0	58	0.54	5	7.1	1.2
10.0	81	0.70	6	2.7	0.0
15.0	76	0.67			
20.0	48	0.49	7	0.6	0.2
30.0	49	0.49	8	0.4	
40.0	54	0.53			
50.0	55	0.53			

These gas analysis data were not deemed good enough for any mass balance information but were used only for exploration. That is, a (CO + CH_4) production maximum appeared about 2 min. after the charge was dropped, and a CO_2 production maximum followed about 5 min. later. The slow combustion technique was imperfect. It is possible that there were leaks in the sample bottles.

TABLE VI

Flow of Outlet Gases vs. Time on Run 7

400 g. charge 7.2% moisture (wet basis)

Temperature of Fluidized Bed
Thermocouple No. 3 Top of Bed 422°-424° C.
Thermocouple No. 4 Bottom of Bed 390°-392° C.
Atmospheric Pressure 740 mm. Hg.
Atmospheric Temperature 80° F.
Gauge Pressure on Rotameter 76 mm. Hg. (estimated).

Time (min.)	Rot. Rdg. (mm.)	Uncorrected C.F.M.	Time (min.)	Rot. Rdg. (mm.)	Uncorrected C.F.M.
2.00	55	0.535	16.00	81	0.700
2.50	65	0.600	17.50	78	0.680
3.00	75	0.663	18.00	79	0.688
4.00	73	0.650	19.16	77	0.675
4.50	71	0.638	20.00	77	0.675
5.00	71	0.638	20.50	75	0.663
6.00	74	0.656	21.00	77	0.675
6.50	75	0.663	21.50	76	0.670
7.00	73	0.650	22.00	75	0.663
7.50	75	0.663	22.50	75	0.663
8.00	75	0.663	23.00	74	0.656
8.50	76	0.670	23.50	74	0.656
9.00	72	0.643	24.00	73	0.650
9.50	76	0.670	24.50	73	0.650
9.83	75	0.663	25.00	72	0.643
10.82	74	0.656	25.50	72	0.643
12.50	81	0.700	26.00	71	0.638
13.00	82	0.705	26.50	71	0.638
13.50	80	0.693	27.50	71	0.638
14.00	75	0.663	28.00	72	0.643
14.50	78	0.680	28.50	71	0.638
15.00	79	0.688	29.00	71	0.638
15.50	80	0.693	29.50	71	0.638

TABLE VI (continued)

Sampling Time (min.) Begin	End	Spl. No.	% CO_2	% CO[1]	% CH_4
2.34	3.00	1	0.2	4.6	3.0
3.00	3.34	2	0.1	12.5	
4.00	4.58	3	0.1	2.6	
		3'		3.0	
5.00	5.34	4	0.4		
6.67	7.30	5	3.2	[1.3]	
8.39	8.67	6	3.9	[0.7]	
10.00	10.50	7	3.5	[0.0]	
11.80		8	3.9	[0.0]	
13.32	14.10	9	3.2	[0.6]	
16.67	17.17	10	1.8	0.0	0.5
20.00	20.44	11	1.2	0.5	5.0

[1] Analysis leaks were eliminated. The CO analyses within brackets were done by HCl - Cu_2Cl_2 absorption and greater accuracy is expected. Slow combustion on samples 10 and 11 was done with better technique than on samples 1, 2, 3, and 3'.

Nitrogen Rates

			Orifice Rdg.	Rot. Rdg.	C.F.M.
Run 6	Beginning	Inlet N_2	9.1 in. H_2O		0.66
		Outlet N_2		69 mm.	0.63
	End	Inlet N_2	9.1 in. H_2O		0.66
		Outlet N_2		69 mm.	0.63
Run 8		Inlet N_2	9.1 in. H_2O		0.66
		Outlet N_2		70 mm.	0.63

The uncorrected N_2 rate out for Run 7 was assumed to have been 0.63 C.F.M. This procedure is justified because Runs 6, 7, and 8 were made in sequence on the afternoon of August 10, 1950.

TABLE VII

August 10, 1950

Analysis Data for CO_2 by Absorption on Run 7

Spl. No.	13	18	17	16	15	14	7
Time (min.)	0.00	4.00	5.33	6.67	10.00	16.67	29.67
Ali.Wt.(g.)	2.908	1.304		1.349	1.367	6.766	1.319
Acid to pH = 4.1 (meq.)	23.3	8.5	17.8	8.9	8.9	43.8	8.6
Acid from pH 8.3-4.1 (meq.)	0.16	0.09	0.15	0.11	0.22	2.04	0.50

As an absorbent, 700 ml. of a solution about 40% KOH by weight was added to a scrubbing column. The solution weighed 1024.5 g. The seven samples removed during operation were estimated to weigh about 10 g. each.

TABLE VIII

Charcoal Sorbate Recovery Data on Runs 5, 6, 7, 8, and 9

Can No.	Sorb. (g.)	Vapors (g.)	Run No.	Sorb. (g.)	
(First desorption)					
			5	21	
2	22		6	36	
3	8		7	39	
4	32		8	23	
	62	44		119	Total except for Run 9
(Second desorption)				150	Total with Run 9
1	22				
5	31		9	31	By difference
6	35				
	88	35			

150 - 79 = 71 g. sorbate lost

$$\frac{\text{Vapor Wt.}}{\text{Sorb. Wt.}} = \frac{79}{150} = 0.527$$

Vapors are recoverable sorbate. The charcoal was desorbed by heating to 140° C. in a vacuum oven, lowering the absolute pressure to 4 mm. Hg. Two cold traps were used in series, No. 1 using dry ice and methyl ethyl ketone, No. 2 using liquid nitrogen.

A white solid plugged the inlet tube of trap No. 2 midway during both desorptions. Upon being warmed to room temperature, the white solid appeared to sublime and left an odorous deposit too small to weigh. Lack of foresight prevented weighing the white solid by difference.

Considerable gas boiled away from trap No. 1 while being warmed to room temperature. This loss was not determined directly. The recovered sorbate (vapor) was water white turning a pale yellow in six months.

TABLE IX

Distillation Data on Vapor

For Runs 1 and 2, 46 g. of vapors were distilled in a Vigreaux column 12 in. high

Temp. (°C.)	Wt. (g.)	Density (g./ml.)	
64.6 - 84.6	6.50	0.76	
			46.00
84.6 - 99.8	9.34		38.78
			7.22 g. lost from small reflux condenser
99.8	22.59		
tar	0.35		6.5 / 46.0 = 14.1% crude methanol
	38.78 g.		

The temperature of the condensing water was often 30° C. This would explain the loss of volatiles such as methyl formate (B. P. = 33° C.).

TABLE X

Distillation Data on Liquid

484 g. combined liquid for Runs 3, 3', 4, 5, 6, 7, 8, and 9 were added to 5 ml. aerosol to wet condenser. Roughly 5 ml. were lost at the beginning because of "free" reflux.

Still pot 110° C.	Product B.P.(°C.)	Takeoff (ml.)	Color
	60.0 - 61.4	0.7	yel. gn.
	61.4 - 64.6	0.5	yel. gn.
	64.6 - 71.2	0.75	yel. gn.
	71.2 - 80.5	0.85	yel. gn.
Started Reflux Ratio of about 40/1	82.0 - 90.0	1.2	
	90.0 - 96.2	1.9	
	96.2 - 97.0	0.35	
Two phases separated	96.8 - 98.0	1.3 bottom 2.2 top	

Bottom phase B.P. 90.4)
Top phase B.P. 94.8) By capillary tube method

Continued distillation continued to yield product which separated into two phases. The material in the column immediately below was mostly acetic acid, from the smell. An accident with the still pot prevented carrying out the distillation further.

The heavier layer gave the spot tests for an aliphatic carbonyl group and strongly decolorized bromine. No reagents were available for the ester test. This layer also contained acids (formic probably) and alcohols. Large quantities of 2,4 dinitrophenylhydrazine derivative was precipitated following the procedure in Fuson and Snyder. Isovaleraldehyde was a possibility, but upon attempting cold alkaline permanganate oxidation, large quantities were consumed and no isovaleric acid odor could be detected, or any of the odors of butyric acid, etc. Formic acid odor, of course, almost completely disappeared leaving a sweet odor.

TABLE X (continued)

From the following boiling points and the preceeding data, it was concluded that the material was 2,5 dimethyl furan.

Allyl acetate	103° C.	
Isobutyl formate	98° C.)	
Adipaldehyde	92-94° C.)	Heavier than water.
2,5 Dimethyl Furan	95° C.)	

APPENDIX B

Sample Calculations

All calculations are based on 100 g. dry sawdust.

1. Nomenclature used in Sample Calculations

(a) Symbols

A' - Acid yield as acetic in liquid by time θ.

$\Delta A'$ - Increment of acid yield as acetic in liquid during time θ.

A'' - Acid yield as acetic in vapor by time θ.

$\Sigma A''$ - Total acid yield as acetic in vapor by the end of the run.

A - Acid yield as acetic at time θ ($A = A' + A''$).

ΔA - Increment of acid yield as acetic produced during the time interval $\Delta\theta$.

C'_A - Weight fraction of acid as acetic in ΔR.

C''_A - The average weight fraction of acid as acetic in ΣV.

C'_M - Weight fraction of methanol in ΔR.

C''_M - The average weight fraction of methanol in ΣV.

D - Mist deposited in the mist cup and glass wool at time θ.

ΣD - Mist deposited in the mist cup and glass wool by the end of the run.

g - Gravitational constant.

G_T - Total gas rate per 100 g. dry sawdust at the outlet at time θ.

G_N - Average of outlet nitrogen rates before start and after close of run per 100 g. dry sawdust.

L - Liquid yield at time θ ($L = R + D$).

M' - Methanol yield in the liquid at time θ.

$\Delta M'$ - Increment of methanol yield in the liquid by time θ.

M'' - Methanol yield in the vapor at time θ.

$\Sigma M''$ - Total methanol yield in the vapor by the end of the run.

M - Methanol yield at time θ ($M = M' + M''$).

ΔM - Increment of methanol yield produced during the time interval $\Delta\theta$.

p - Pressure.

q - Volumetric gas rate at actual conditions through rotameter.

q_o - Volumetric gas rate for gas at 760 mm. Hg. and 70° F.

R - Condensate recovered in the condenser receiver by time θ.

ΔR - Increment of condensate produced during the time interval $\Delta\theta$.

ΣR - Condensate recovered in the condenser receiver by the end of the run.

S - Sorbate (charcoal pickup) at time θ (sorbate loss = $S - V$).

S_f - Cross section of rotameter float.

S_o - Cross sectional area of constriction between rotameter tube and float at one particular float position (reading).

ΣS - Total sorbate for Runs 5, 6, 7, 8, and 9.

u - Average velocity of gases through rotameter constriction.

V - Vapor yield at time θ.

v_f - Volume of rotameter float.

ΔV - Increment of vapor produced during time interval $\Delta\theta$.

ΣV - Total vapor for Runs 5, 6, 7, 8, and 9.

W - Sawdust charged.

X - Carbon dioxide rate at time θ.

Y - Carbon monoxide rate at time θ.

Z - CO_2 content of absorbent at time θ.

ρ - Density of gases.

ρ_f - Density of rotameter float.

(b) Abbreviations

Abs. - Absorbent

Absn. - Absorption

Ali. - Aliquot

C.F.M. - Uncorrected gas rate in ft^3/min. obtained directly from the correlation of rotameter reading vs. gas rate at 70^o F. and 760 mm. Hg.

Cond. - Condensate

No. - Number

Rdg. - Reading

Rot. - Rotameter

Sorb. - Sorbate

Spl. - Sample

pT - pH at end point

2. Sample Calculation of Liquid Yield vs. Time

$$L = R \frac{\Sigma R + \Sigma D}{\Sigma R} (100/0.928\ W)$$

Run 6 Time 0.50 min.

$R = 4.16$ g.
$\Sigma D = 19.5$ g.
$\Sigma R = 113.7$ g.
$W = 442$ g.

$$L = 4.16 \frac{113.7 + 19.5}{113.7} (100/0.928\ 442) = 1.19 \text{ g./100 g.}$$

3. Sample Calculation of Vapor Yield vs. Time

$$V = S \frac{\Sigma V}{\Sigma S} (100/0.928\ W)$$

Run 6 Time 1.00 min.

$\Sigma S = 150$ g.
$\Sigma V = 79$ g.
$W = 442$ g.
$S = 7$ g.

$$V = 7 \frac{79}{150} (100/0.928\ 442) = 0.90 \text{ g./100 g.}$$

4. Calculation of Total Liquid

The curves of liquid and vapor in Fig.'s 1 and 2 were added graphically.

5. Sample Calculation of Increments of Yields of Acid as Acetic and of Methanol vs. Time in the Liquid

$$\Delta A' = C'_A \, \Delta R \, \frac{\Sigma R + \Sigma D}{\Sigma R} \, (100/0.928 \, W)$$

$$\Delta M' = C'_M \, \Delta R \, \frac{\Sigma R + \Sigma D}{\Sigma R} \, (100/0.928 \, W)$$

Run 6 Time 1.00 min.

$C'_A = 0.184$

$C'_M = 0.0268$

$\Delta R = 32.4$ g.

$\Sigma D = 19.5$ g.

$\Sigma R = 113.7$ g.

$W = 442$ g.

$$\Delta A' = 0.184 \; 32.4 \, \frac{113.7 + 19.5}{113.7} \, (100/0.928 \; 442)$$

$= 5.89$ g./100 g.

$$\Delta M' = 0.0268 \; 32.4 \, \frac{113.7 + 19.5}{113.7} \, (100/0.928 \; 442)$$

$= 0.248$ g./100 g.

6. Sample Calculation of Yields of Acid as Acetic and of Methanol vs. Time in the Vapor

$$A'' = C''_A \, V$$

$$M'' = C''_M \, V$$

6. (continued)

Run 6 Time 1.00 min.

$C''_A = 0.0161$

$C''_M = 0.0828$

$V = 0.90$ g./100 g.

$A'' = 0.0161\ 0.90 = 0.0145$ g.

$M'' = 0.0828\ 0.90 = 0.0737$ g.

7. Calculation of Acid Yield as Acetic

The curves of HOAc in the liquid and HOAc in the vapor were added graphically in Fig.'s 3 and 4.

8. Calculation of Methanol Yield

The curves of HOMe in the liquid and HOMe in the vapor were added graphically in Fig.'s 5 and 6.

9. Sample Calculation of Outlet Gas Rate vs. Time

$$G_T = (\text{C.F.M.}\ \frac{q}{q_o}\ \frac{28.3(\text{l./ft}^3)}{\text{g. mol vol.}}\ \frac{100}{0.928\ \text{W.}}\ \frac{\text{g.mol/min.}}{100\ \text{g.}}$$

Rotameter Correction Factor (q/q_o)

From $S_f(p_1-p_2) = v_f(\rho_f-\rho)$, a force balance, and $\frac{u^2}{2g} = C^2\ \frac{(p_1-p_2)}{\rho}$, the orifice energy equation, and $u = q\ S_o$, there results

$$q/\sqrt{\rho} = CS_i\ [\frac{2gv_f(\rho_f-\rho)}{S_f}]^{1/2}.$$

C is a constant for a single fluid over a wide range of rates, $(\rho_f-\rho)$ can be assumed equal to ρ_f for gases, and S_i is a constant for any particular rotameter reading; i.e., float position. Hence for any one rotameter reading

$$q/q_o = [\rho_o/\rho]^{1/2}.$$

Rot. Calibration Conditions -- 70° F. and 760 mm. Hg.

Run 7 Time 7.00 min.

pres. in Rot. = 816 mm. Hg.
room temp. = 80° F.
C.F.M. = 0.650 ft³/min.
W = 400 g.

$$\text{g. mol vol.} = 22.4\ \frac{760}{816}\ \frac{540}{492} = 22.9\ \text{l.}$$

$$\frac{q}{q_o} = [\frac{760}{530}\ \frac{540}{816}]^{1/2} = 0.974$$

$$G_T = 0.650\ 0.974\ \frac{28.3}{22.9}\ \frac{100}{0.928\ 400} = 0.650 \times 0.324$$

$$= 0.2105\ \text{g. mol/min. 100 g.}$$

9. (continued)

The outlet N_2 rate for Run 7 was estimated from measurements made during Runs 6 and 8. Hence, a different rotameter correction was needed. The only difference in conditions was a difference in pressure on the rotameter. During Runs 6 and 8 there was only atmospheric pressure on it, but for Run 7 a scrubbing tower was added on between the rotameter and the outlet.

Conditions during Runs 6 and 8

pres. in Rot. = 740 mm. Hg.
room temp. = 80° F.
C.F.M. = 0.63 ft^3/min.

$$\text{g. mol vol.} = 22.4 \frac{760}{740} \frac{540}{492} = 25.2 \text{ l.}$$

$$\frac{q}{q_o} = \left[\frac{760}{530} \frac{540}{740}\right]^{1/2} = 1.023$$

Nitrogen flow for Runs 6, 7, and 8

$$= 0.63 \; 1.023 \frac{28.3}{25.2}$$

$$= 0.723 \text{ g. mol/min.}$$

W (Run 7) = 400 g.

$$G_N \text{ (Run 7)} = 0.723 \frac{100}{0.928 \; 400} = 0.195 \text{ g. mol/min. 100 g.}$$

10. Calculation of Gas Evolved

The smoothed curve in Fig. 8 was integrated graphically.

11. Sample Calculation of Rates of CO_2 and CO by Gas Analysis

Run 7 Time 6.98 min.

$$X = G_T \left(\frac{\%CO_2}{100}\right)$$

$$Y = G_T \left(\frac{\%CO}{100}\right)$$

G_T = 0.211 g. mol./min. (see Fig. 7)

$\%CO_2$ = 3.2

$\%CO$ = 1.3

$$X = 0.211 \left(\frac{3.2}{100}\right) = 0.00675 \text{ (g. mol./min.)}$$

$$Y = 0.211 \left(\frac{1.3}{100}\right) = 0.00274 \text{ (g. mol./min.)}$$

12. Calculation by Gas Analysis of the Yields of CO_2, CO, and [Total Evolved Gas - (CO_2 + CO)]

Curves in Fig. 9 were integrated graphically.

13. Sample Calculation of CO_2 Yield vs. Time by Absorption

$$Z = \left(\frac{KHCO_3}{K^+}\right)\left(\frac{K^+}{Ali.\ Wt.}\right)^1 \text{Abs. Wt.} \frac{100}{W\ 0.928}$$

$KHCO_3$ = meq. acid from pH = 8.3 to pH = 4.1 for aliquot
K^+ = meq. acid from pH = 14 to pH = 4.1 for aliquot
Abs. Wt. = Orig. Abs. Wt. - Spl. Wt. x No. Spls. removed

Run 7	Time (min.)	$KHCO_3$ (meq.)	K^+ (meq.)	Abs.Wt. (g.)	$\frac{K^+}{Ali.Wt.}\left(\frac{meq.}{g.}\right)$
W = 400 g.	0.00	0.16	23.3	1024	6.53
	6.67	0.11	8.9	994	6.53

Time (min.)

0.00 $Z = \frac{0.16}{23.3}\ 6.53\ 1024\ \frac{100}{400\ 0.928} = 0.0124$ g.mol. CO_2 Blank

6.67 $Z = \frac{0.11}{8.9}\ 6.53\ 994\ \frac{100}{400\ 0.928} = 0.0216$ g.mol. CO_2

$Y = Z - 0.0124 = 0.0092$ g. mol. CO_2

[1] The ratio of total potassium ion to the weight of absorbent was assumed to be a constant. The values actually calculated were:

Spl. No.	13	18	17	16	15	14	7
$\left(\frac{K^+\ meq.}{Ali.Wt.g.}\right)$	8.02	6.51	None	6.60	6.52	6.48	6.53

The ratio for Spl. 13 was thrown out and the others were averaged (average ratio = 6.53). This average was then employed for all samples.

14. Calculation of Total Liquid Rate vs. Time

Curves of Total Liquid in Fig.'s 1 and 2 were differentiated graphically.

15. Calculation of Acid Rate (as Acetic) vs. Time

Curves of Total HOAc in Fig.'s 3 and 4 were differentiated graphically.

16. Calculation of Methanol Rate vs. Time

Curves of Total HOMe in Fig.'s 5 and 6 were differentiated graphically.

17. Calculation of CO_2 Rate vs. Time by Absorption

The curve of CO_2 Yield vs. Time in Fig. 10 was differentiated graphically.

APPENDIX C

TABLE XI

Overall Yields for Runs 6, 7, and 8

Basis: 100 g. Dry Sawdust

	Run 6 397° C. (g.)	Run 7 406° C. (g.)	Run 8 415° C. (g.)
Net Charge	107.2	107.2	107.2
Liquid	32.3	30.5	32.9
Vapor	4.6	5.5	2.9
Adsorbate gas	4.1	4.9	2.6
CO_2		4.7	
CO		1.5	
CH_4		6.1	
Acid as Acetic	5.9		5.8
Methanol	1.0		1.1
Total liquid - free moisture	29.7	28.8	28.6
Charcoal	17.5	31.6	24.2
Gas		17.2	
Tar and loss		22.4	

TABLE XII

Corrected Yields for Run 6

Basis: 100 g. Dry Sawdust

Spl. No.	Time (min.)	Liq. Yield (g.)	Liq. HOAc Yield (g.)	Liq. HOMe Yield (g.)	Vapor Yield (g.)	Vapor HOAc Yield (g.)	Vapor HOMe Yield (g.)
6	0.50	1.2	0.17	0.036			
5	1.00	10.5	1.87	0.284	0.90	0.0145	0.074
4	2.00	18.3	3.85	0.540			
	3.34				2.70	0.0435	0.224
3	4.00	26.6	5.11	0.807			
	7.50				3.34	0.0538	0.276
2	10.00	31.0	5.72	0.968			
	13.33				3.86	0.0621	0.320
1	30.00	32.5	5.95	1.023	4.62	0.0745	0.382

TABLE XIII

Corrected Yields for Run 8

Basis: 100 g. Dry Sawdust

Spl. No.	Time (min.)	Liq. Yield (g.)	Liq. HOAc Yield (g.)	Liq. HOMe Yield (g.)	Vapor Yield (g.)	Vapor HOAc Yield (g.)	Vapor HOMe Yield (g.)
19	1.00	8.2	1.47	0.214	0.76	0.0122	0.063
8	2.00	18.7	3.46	0.502			
9	3.00	23.8	4.40	0.653			
	3.33				2.16	0.0348	0.178
10	5.17	27.8	5.07	0.783			
	6.67				2.41	0.0388	0.199
11	10.82	31.1	5.58	0.947			
12	30.00	33.0	5.85	1.075	3.18	0.0512	0.263

TABLE XIV

Corrected Gas Rates for Run 7

Basis: 100 g. Dry Sawdust

Time (min.)	Rate of Outlet Gas (g.mol/ min.)	Rate of Outlet Gas-N_2 (g.mol/ min.)	Time (min.)	Rate of Outlet Gas (g.mol/ min.)	Rate of Outlet Gas-N_2 (g.mol/ min.)
2.0	0.173		16.0	0.227	0.032
2.5	0.194		17.5	0.220	0.025
3.0	0.215	0.020	18.0	0.223	0.028
4.0	0.210	0.015	19.2	0.219	0.024
4.5	0.206	0.011	20.0	0.219	0.024
5.0	0.206	0.011	20.5	0.215	0.020
6.0	0.212	0.017	21.0	0.219	0.024
6.5	0.215	0.020	21.5	0.217	0.022
7.0	0.210	0.015	22.0	0.215	0.020
7.5	0.214	0.019	22.5	0.215	0.020
8.0	0.215	0.020	23.0	0.212	0.017
8.5	0.217	0.022	23.5	0.212	0.017
9.0	0.208	0.013	24.0	0.210	0.015
9.5	0.217	0.022	24.5	0.210	0.015
9.8	0.215	0.020	25.0	0.208	0.013
10.8	0.216	0.021	25.5	0.208	0.013
12.5	0.227	0.032	26.0	0.206	0.011
13.0	0.228	0.033	26.5	0.206	0.011
13.5	0.224	0.029	27.5	0.206	0.011
14.0	0.215	0.020	28.0	0.208	0.013
14.5	0.220	0.025	28.5	0.206	0.011
15.0	0.223	0.028	29.0	0.206	0.011
15.5	0.224	0.029	29.5	0.206	0.011

TABLE XV

Corrected CO_2 and CO Rates for Run 7

Basis: 100 g. Dry Sawdust

Spl. No.	Time[1] (min.)	Rate of[2] Outlet Gas (g.mol/ min.)	% CO_2	% CO	Rate of CO_2 (mg.mol/ min.)	Rate of CO (mg.mol/ min.)
1	2.67	0.205	0.2	4.6	0.4	9.4
2	3.17	0.223	0.1	12.5	0.2	28.0
3	4.29	0.206	0.1	2.6	0.2	5.4
3'	4.29	0.206		3.0		6.2
4	5.17	0.206	0.4		0.8	
5	6.98	0.210	3.2	1.3	6.7	2.7
6	8.53	0.217	3.9	0.7	8.5	1.5
7	10.25	0.215	3.5	0.0	7.5	0.0
8	12.10	0.225	3.9	0.0	8.8	0.0
9	13.71	0.217	3.2	0.6	7.0	1.3
10	16.92	0.223	1.8	0.0	4.0	0.0
11	20.22	0.217	1.2	0.5	2.6	1.1
()[3]	30.00	0.206	0.4		0.8	

[1] The average of the time when the sampling was begun and the time when it was completed.

[2] Rate given by smoothed curve in Fig. 8; i.e., (0.195 + Rate of Evolved Gas) g.mol/min.

[3] Spl. No. 12 of Run 7 was accidentally lost and the corresponding analysis from Run 2 was used.

TABLE XVI

Corrected Yields for Run 7

Basis: 100 g. Dry Sawdust

Time (min.)	Gas Anal. CO Yield (g. mol)	Gas Anal. CO_2 Yield (g. mol)	Gas Anal. Total $-(CO_2 + CO)$ (g. mol)	Absn. CO_2 Yield (g. mol)
4.00	0.0271			0.0054
6.67[1]	0.0392	0.0056	0.018	0.0092
10.00	0.0448	0.0320	0.049	0.0302
16.67	0.0480	0.0800	0.177	0.0675
25.00			0.331	
29.67	0.0536	0.1067	0.379	0.0862

[1] The data of Spl. No. 17 (5.33 min.) were not included in the results because they would indicate a loss of CO_2 instead of a gain. They are unreasonable in comparison with the other data.

TABLE XVII

Rates vs. Time

Basis: 100 g. Dry Sawdust

Time (min.)	Total Liquid (g./min.) Runs		Acid as Acetic (g./min.) Runs		Methanol (g./min.) Runs		CO_2 (mg.mol/min.) Absn.
	6	8	6	8	6	8	Run 7
0.5	25		4.5		0.60		
1.0	12	14	2.5	3.0	0.40	0.50	
2.0	6	7	1.0	1.2	0.28	0.24	
4.0	2	2	0.3	0.3	0.08	0.08	
6.0							2.4
8.0	0.6	0.6	0.1	0.1	0.03	0.03	6.0
10.0							7.0
16.0	0.1	0.1					3.5

APPENDIX D

Fig. 1

Corrected Yields for Run 6 vs. Time

Total Liquid

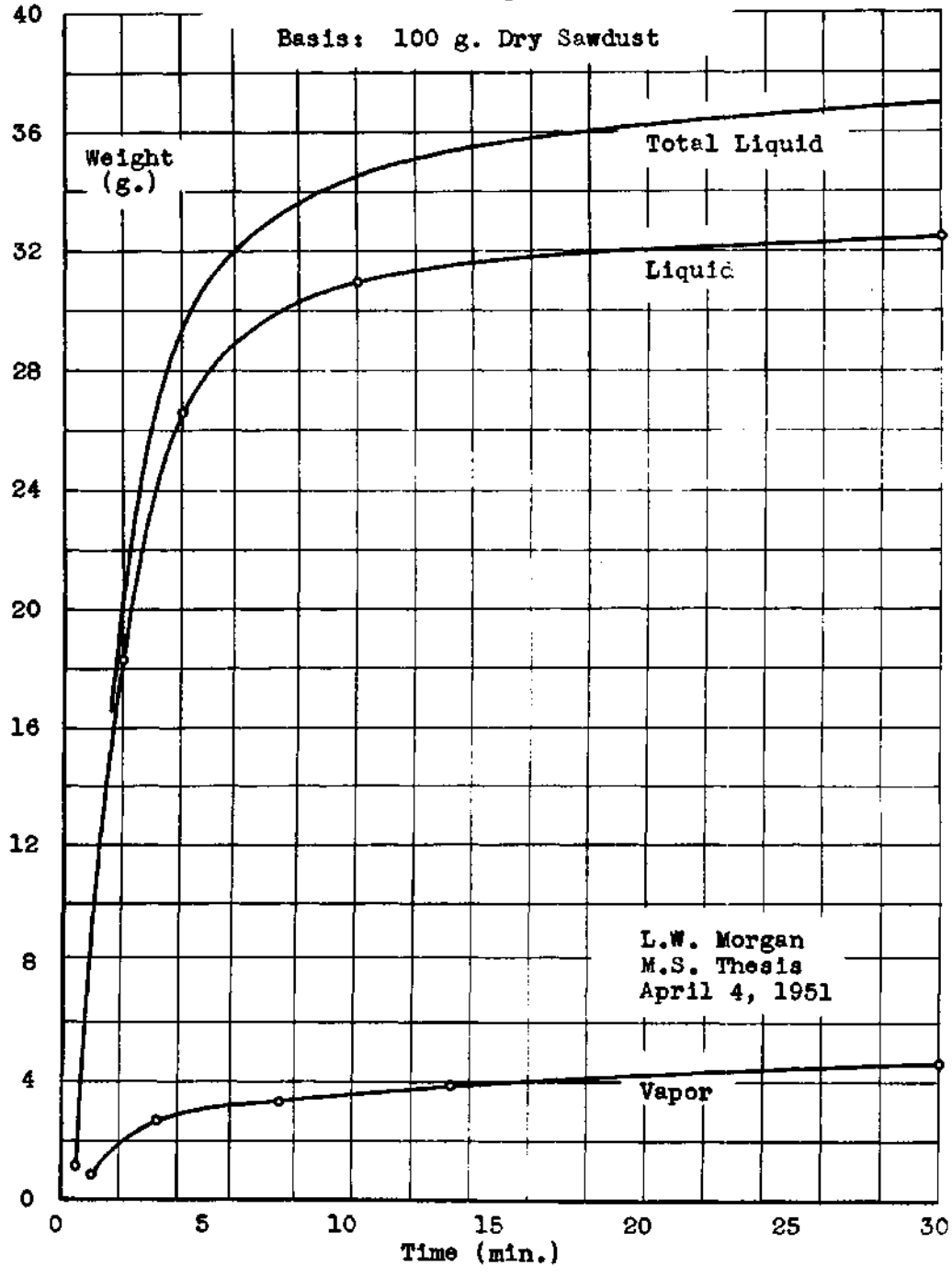

Fig. 2

Corrected Yields for Run 8 vs. Time

Total Liquid

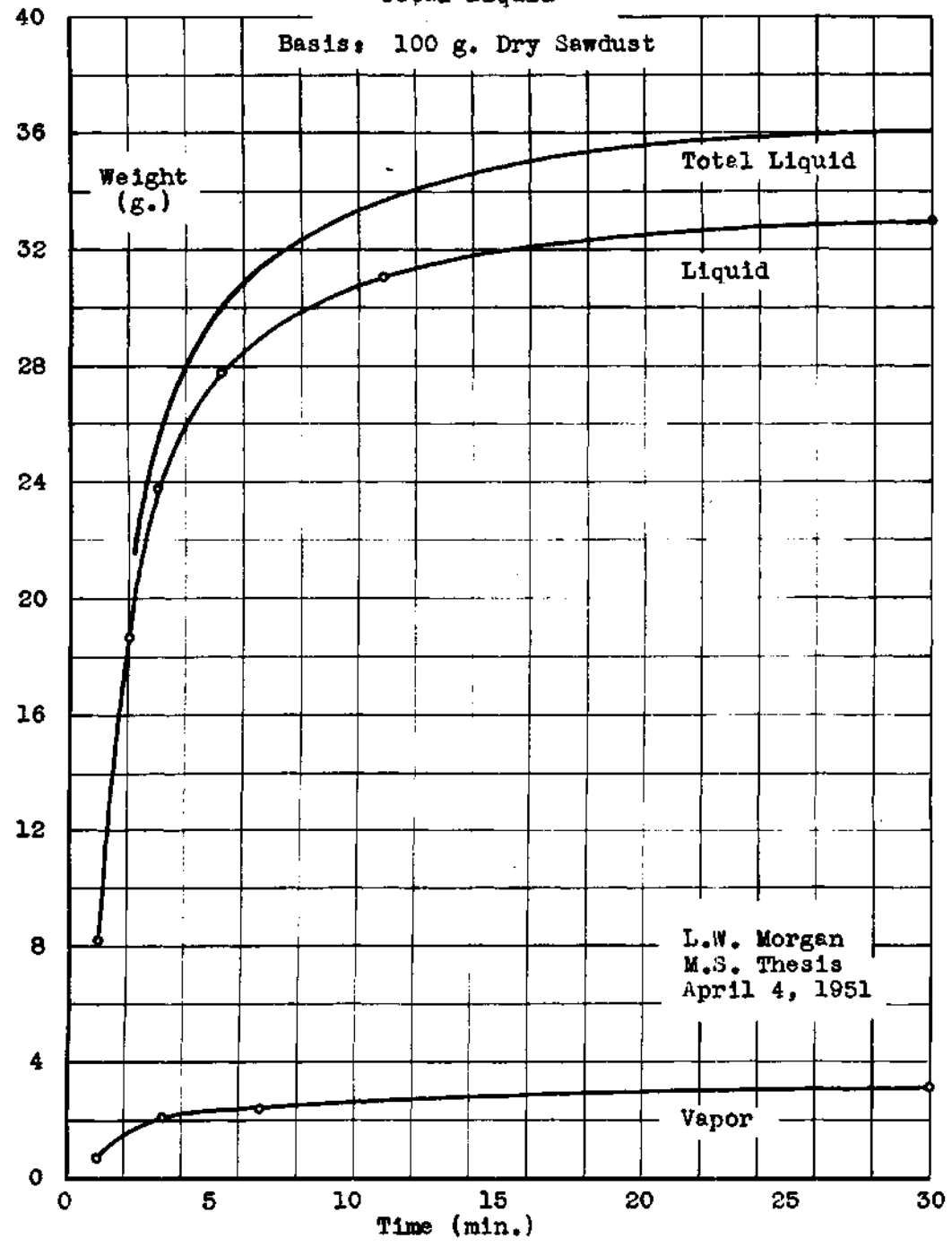

Fig. 3

Corrected Yields for Run 6 vs. Time

Acid as Acetic

Basis: 100 g. Dry Sawdust

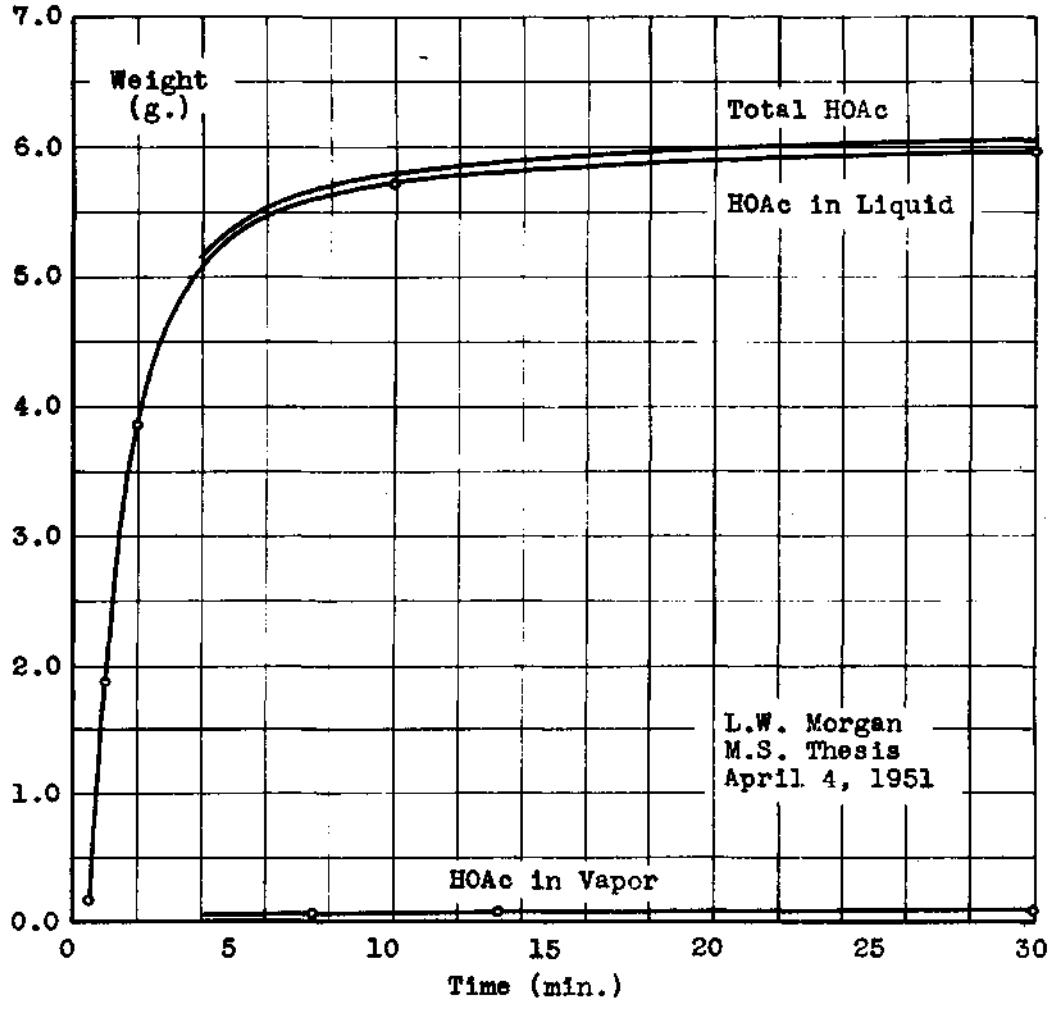

Fig. 4

Corrected Yields for Run 8 vs. Time

Acid as Acetic

Basis: 100 g. Dry Sawdust

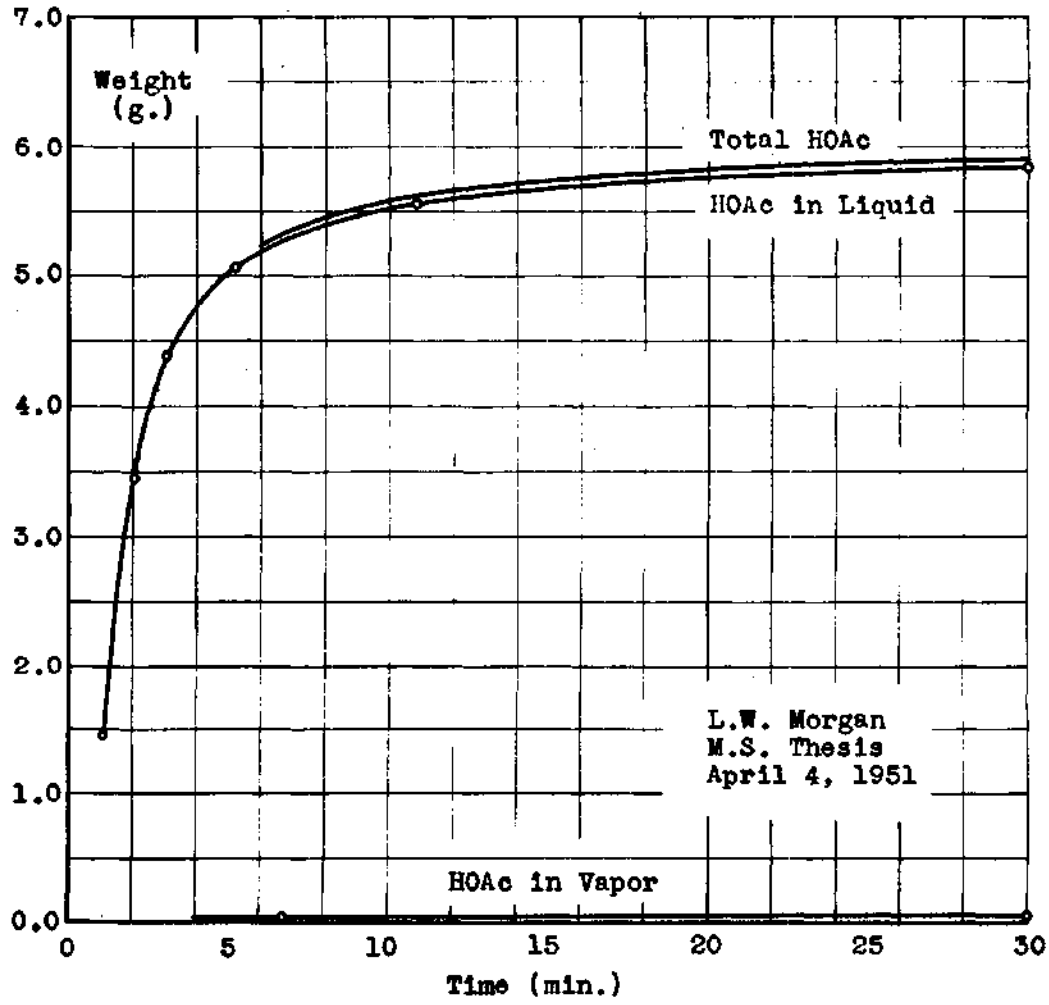

Fig. 5

Corrected Yields for Run 6 vs. Time

Methanol

Basis: 100 g. Dry Sawdust

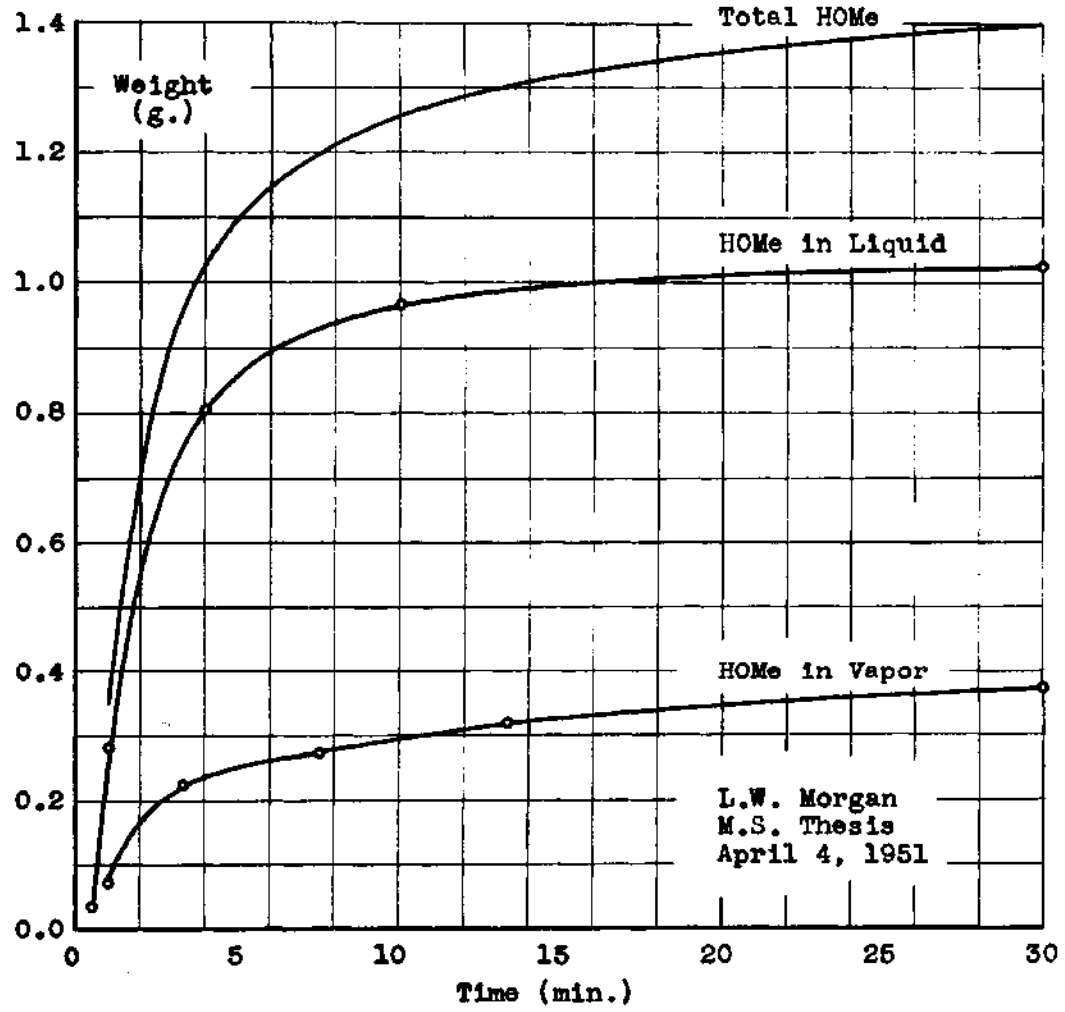

Fig. 6

Corrected Yields for Run 8 vs. Time

Methanol

Basis: 100 g. Dry Sawdust

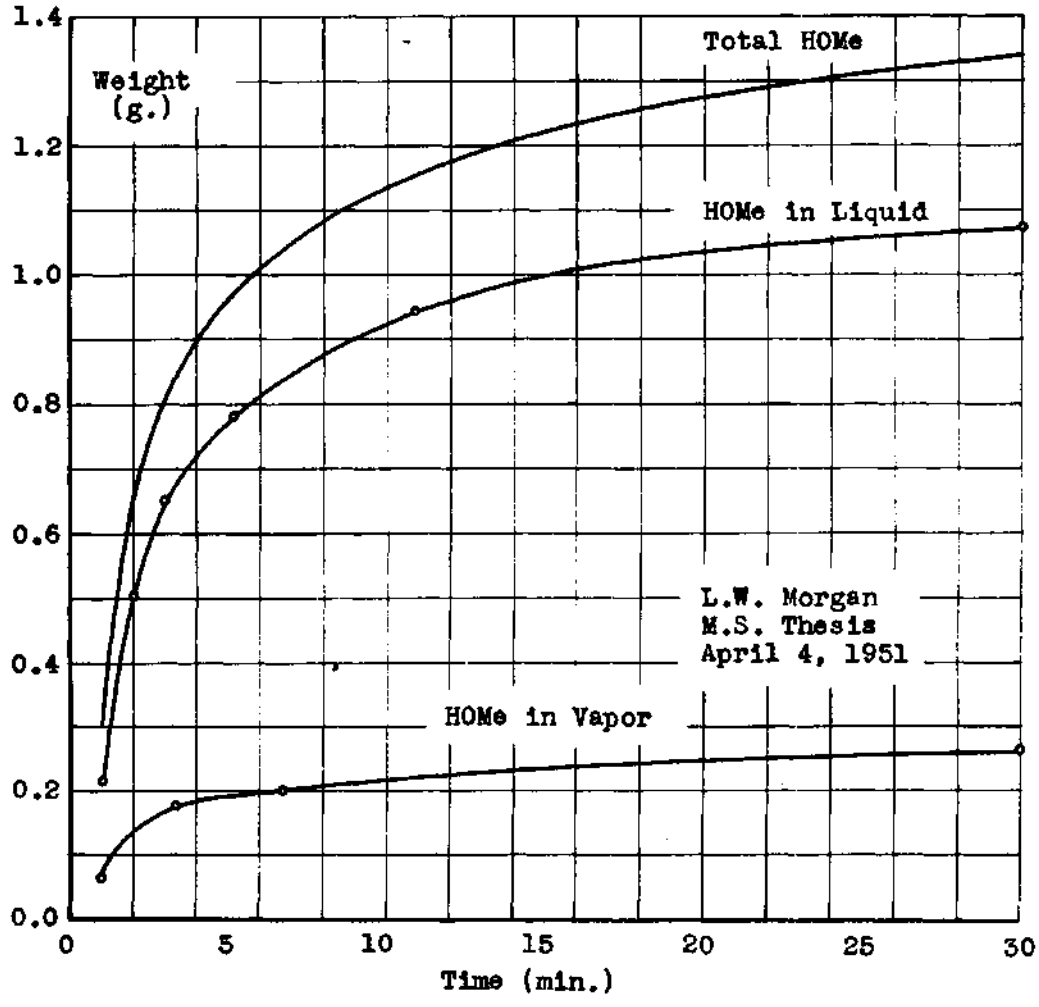

Fig. 7

Outlet Gas Rate vs. Time

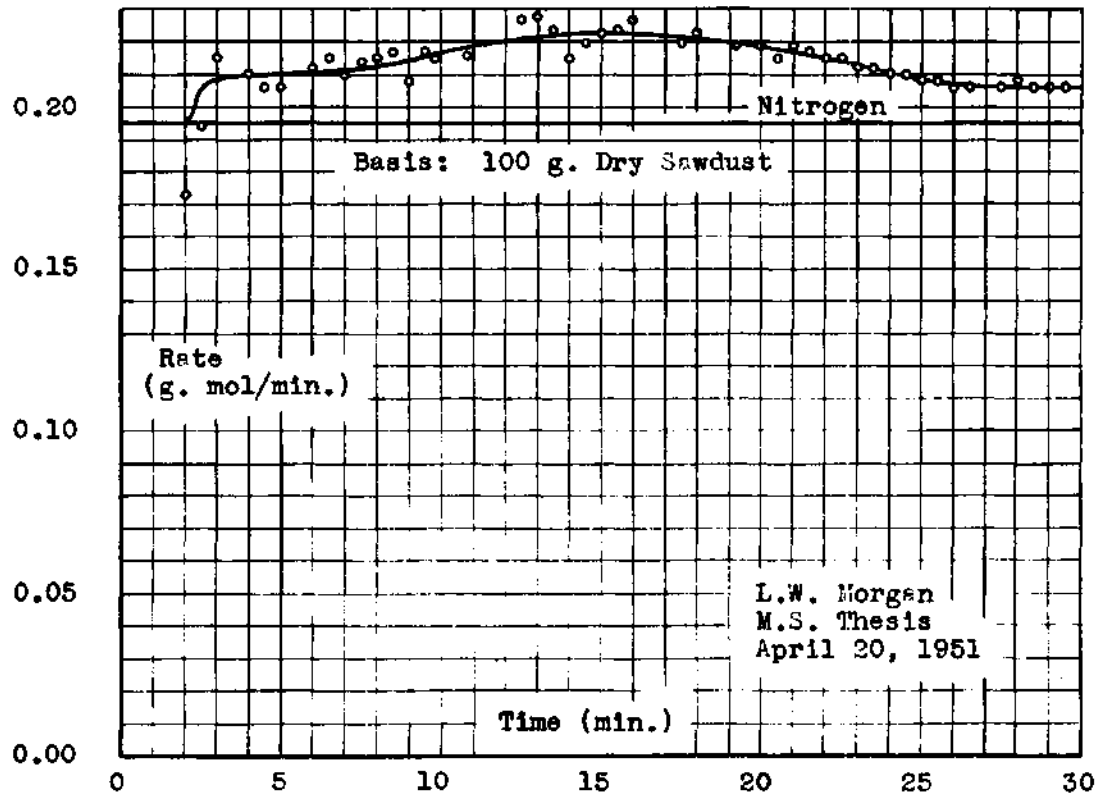

Fig. 8 Evolved Gas Rate vs. Time

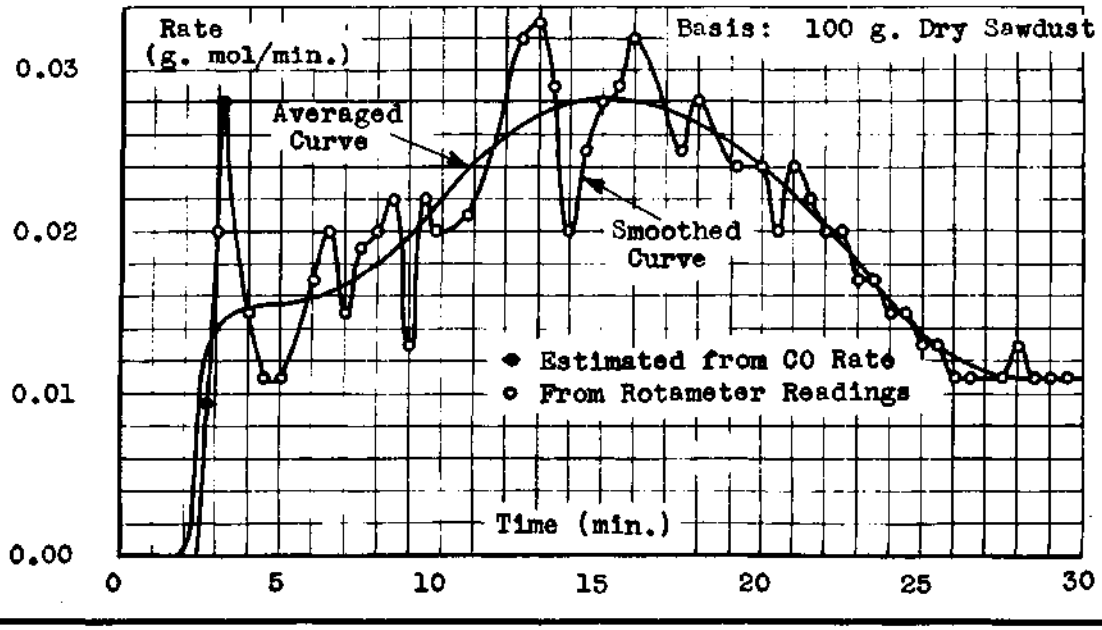

Fig. 9

Gas Rates vs. Time

Basis: 100 g. Dry Sawdust

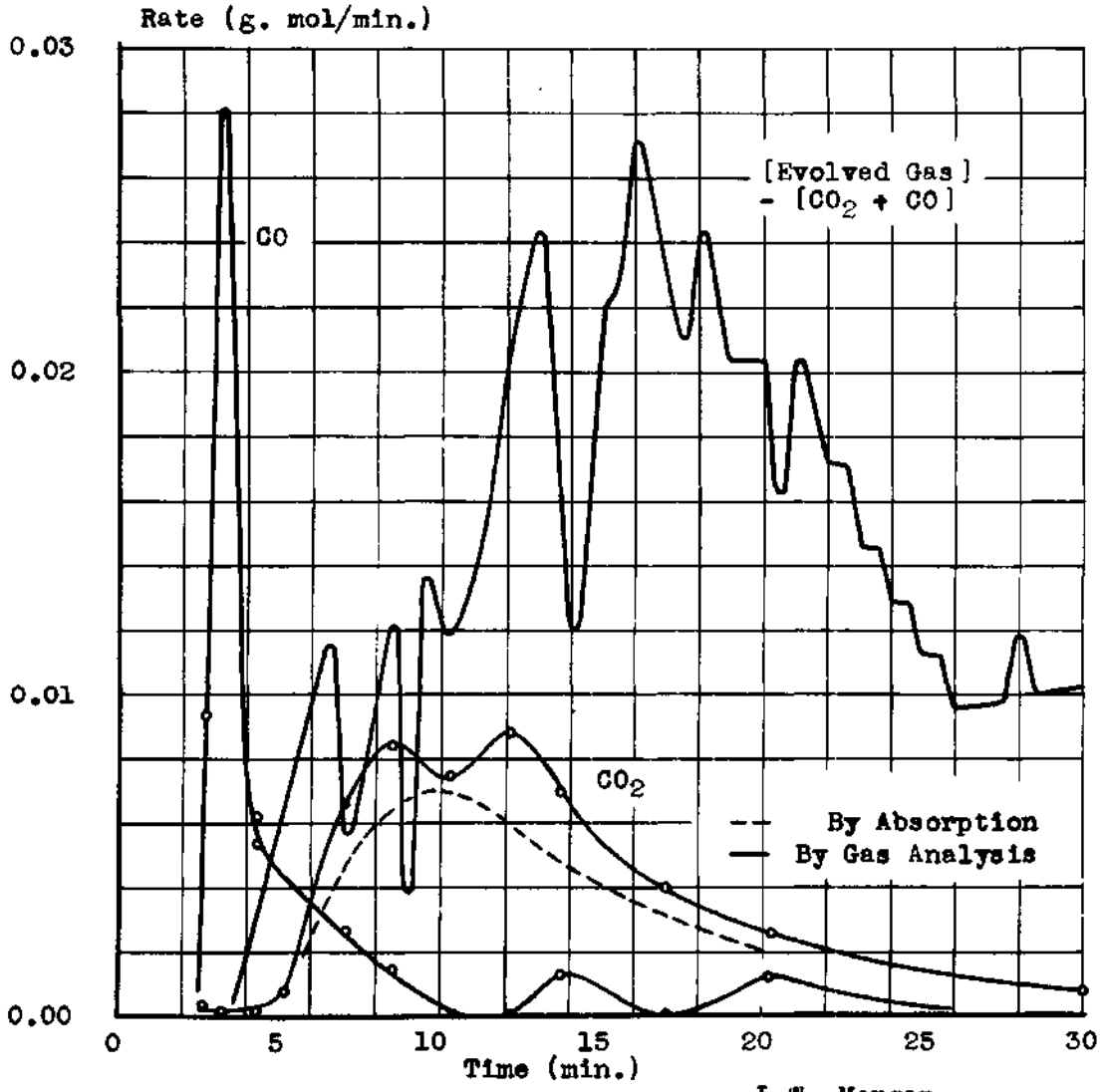

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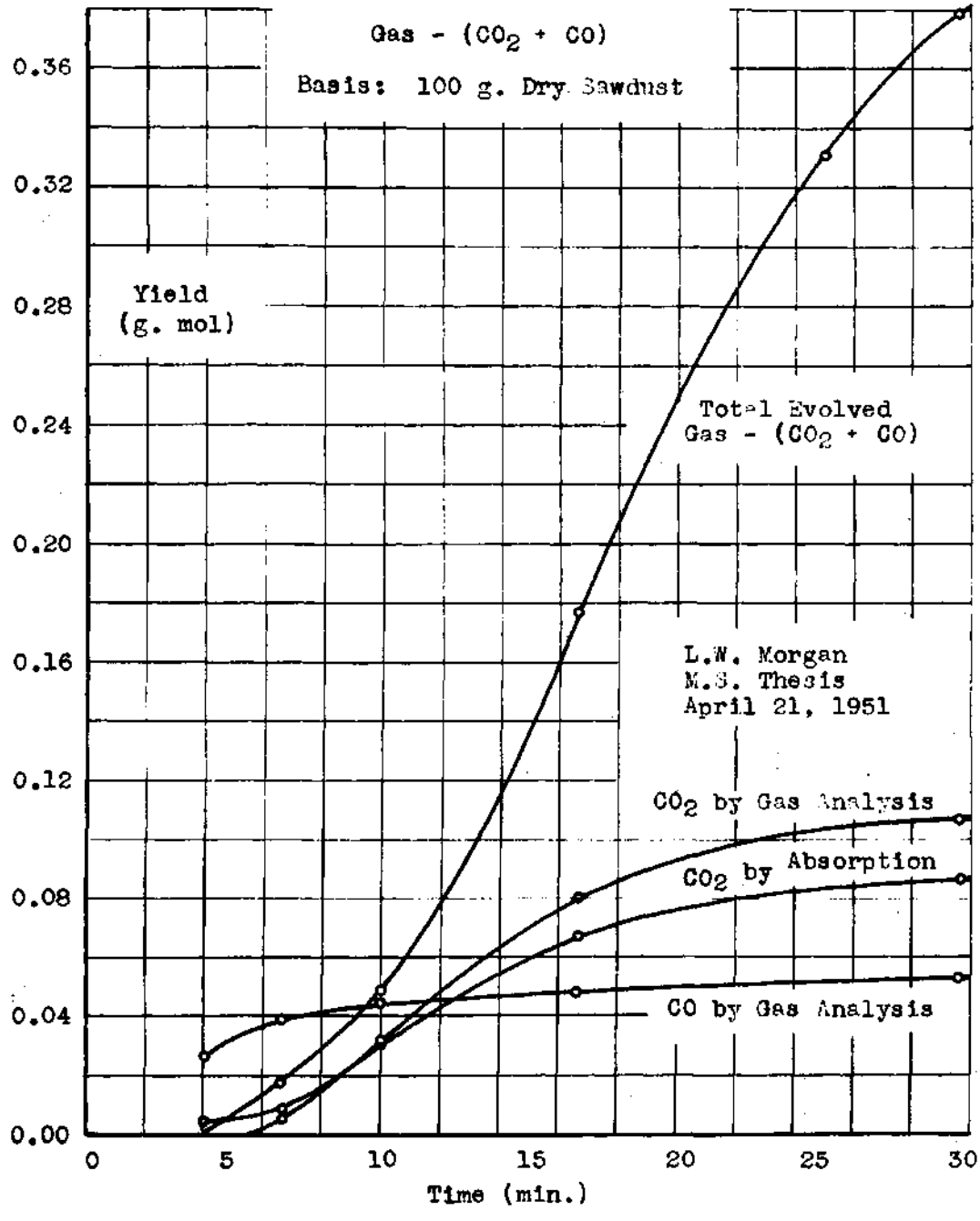
Fig. 10

Corrected Yields for Run 7 vs. Time

CO_2, CO, and Total Evolved

Gas - (CO_2 + CO)

Basis: 100 g. Dry Sawdust



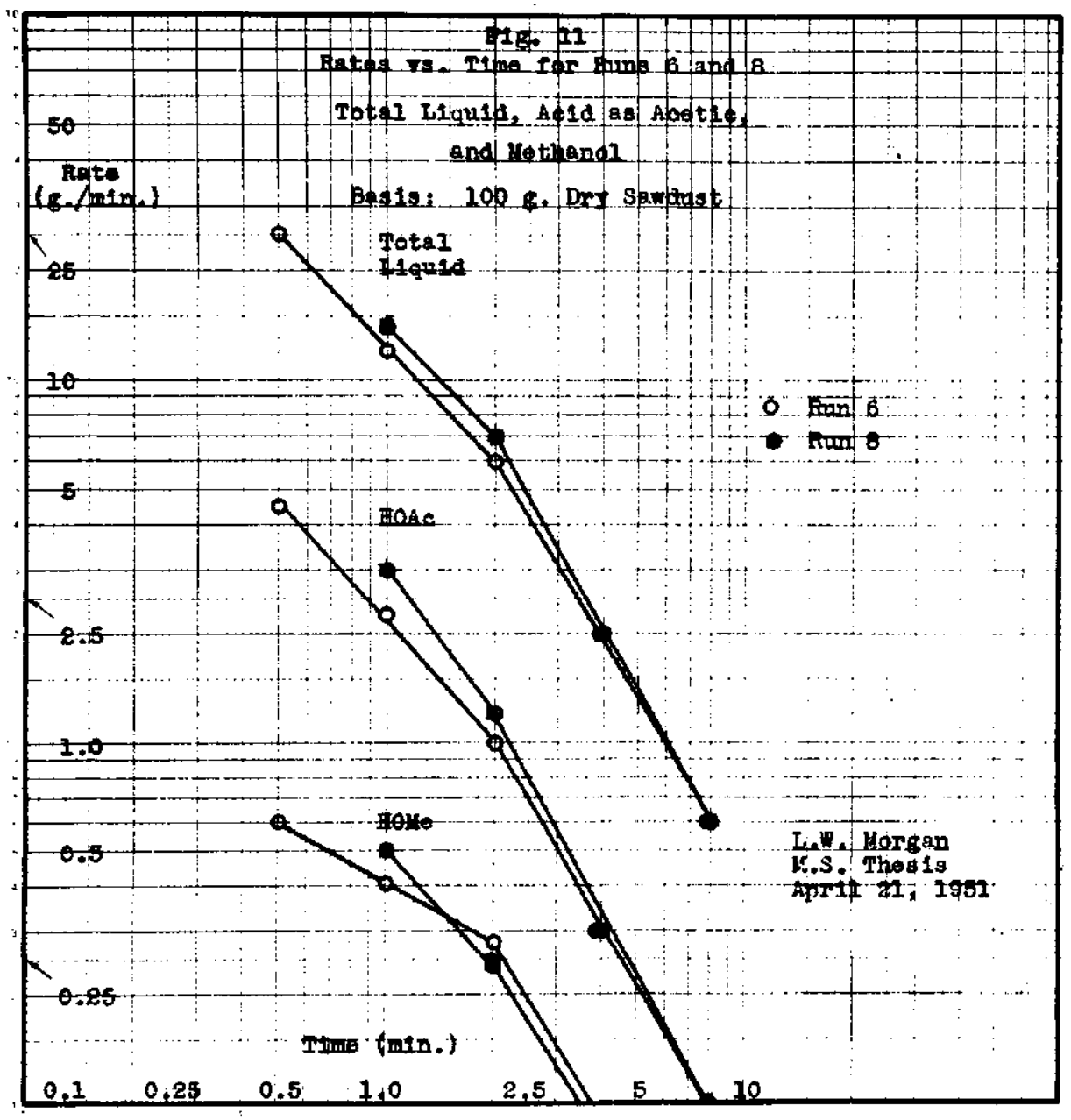


Fig. 11
Rates vs. Time for Runs 6 and 8
Total Liquid, Acid as Acetic,
and Methanol
Basis: 100 g. Dry Sawdust
Rate (g./min.)
50
25
10
5
2.5
1.0
0.5
0.25
Total Liquid
HOAc
HOMe
Run 6
Run 8
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Time (min.)
0.1
0.25
0.5
1.0
2.5
5
10

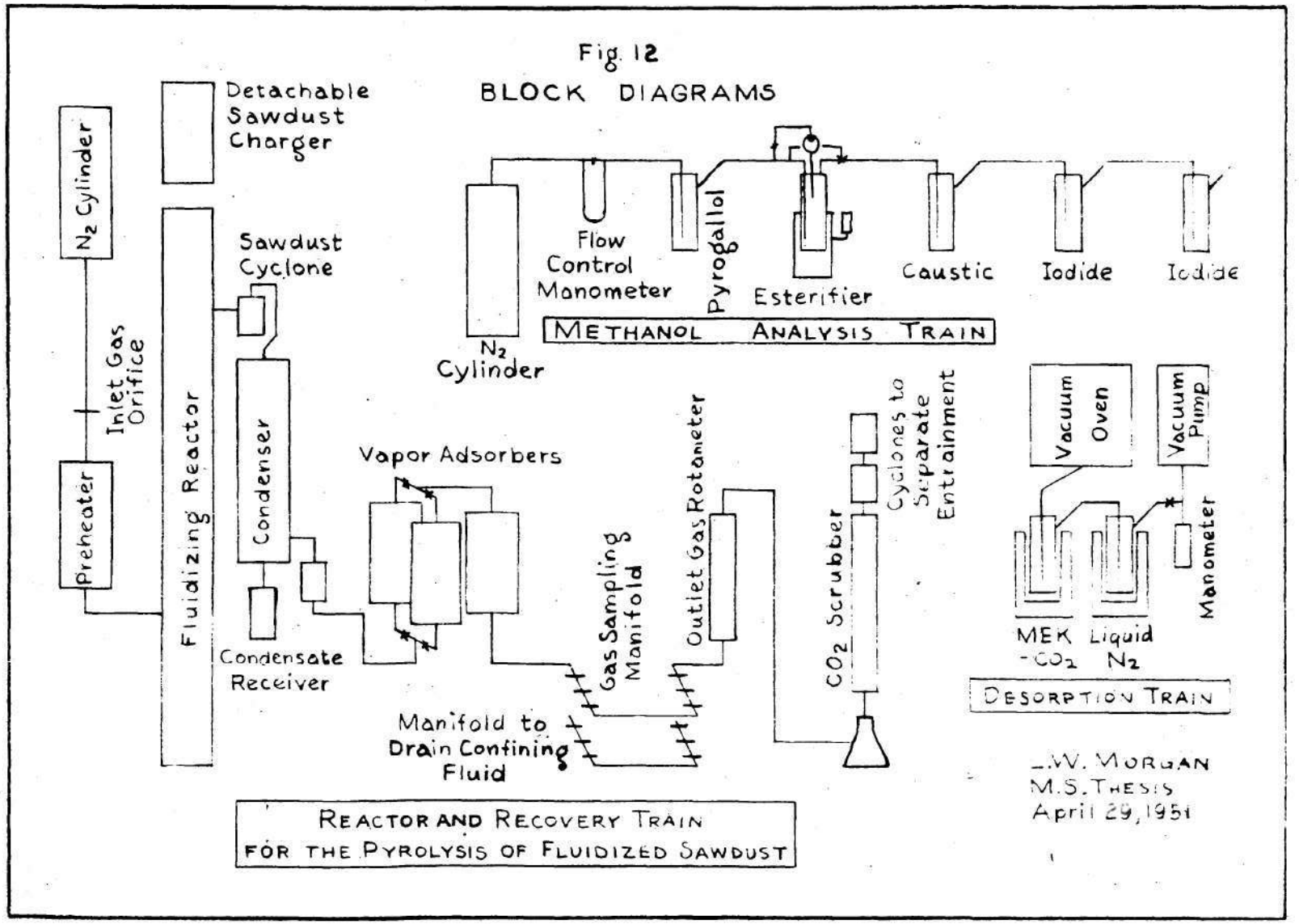
Fig. 12
BLOCK DIAGRAMS
Detachable Sawdust Charger
N2 Cylinder
Sawdust Cyclone
Inlet Gas Orifice
Preheater
Fluidizing Reactor
Condenser
Condensate Receiver
Vapor Adsorbers
Gas Sampling Manifold
Outlet Gas Rotameter
CO2 Scrubber
Cyclones to Separate Entrainment
Manifold to Drain Confining Fluid
REACTOR AND RECOVERY TRAIN FOR THE PYROLYSIS OF FLUIDIZED SAWDUST
N2 Cylinder
Flow Control Manometer
Pyrogallol
Esterifier
Caustic
Iodide
Iodide
METHANOL ANALYSIS TRAIN
Vacuum Oven
Vacuum Pump
Manometer
MEK - CO2
Liquid N2
DESORPTION TRAIN
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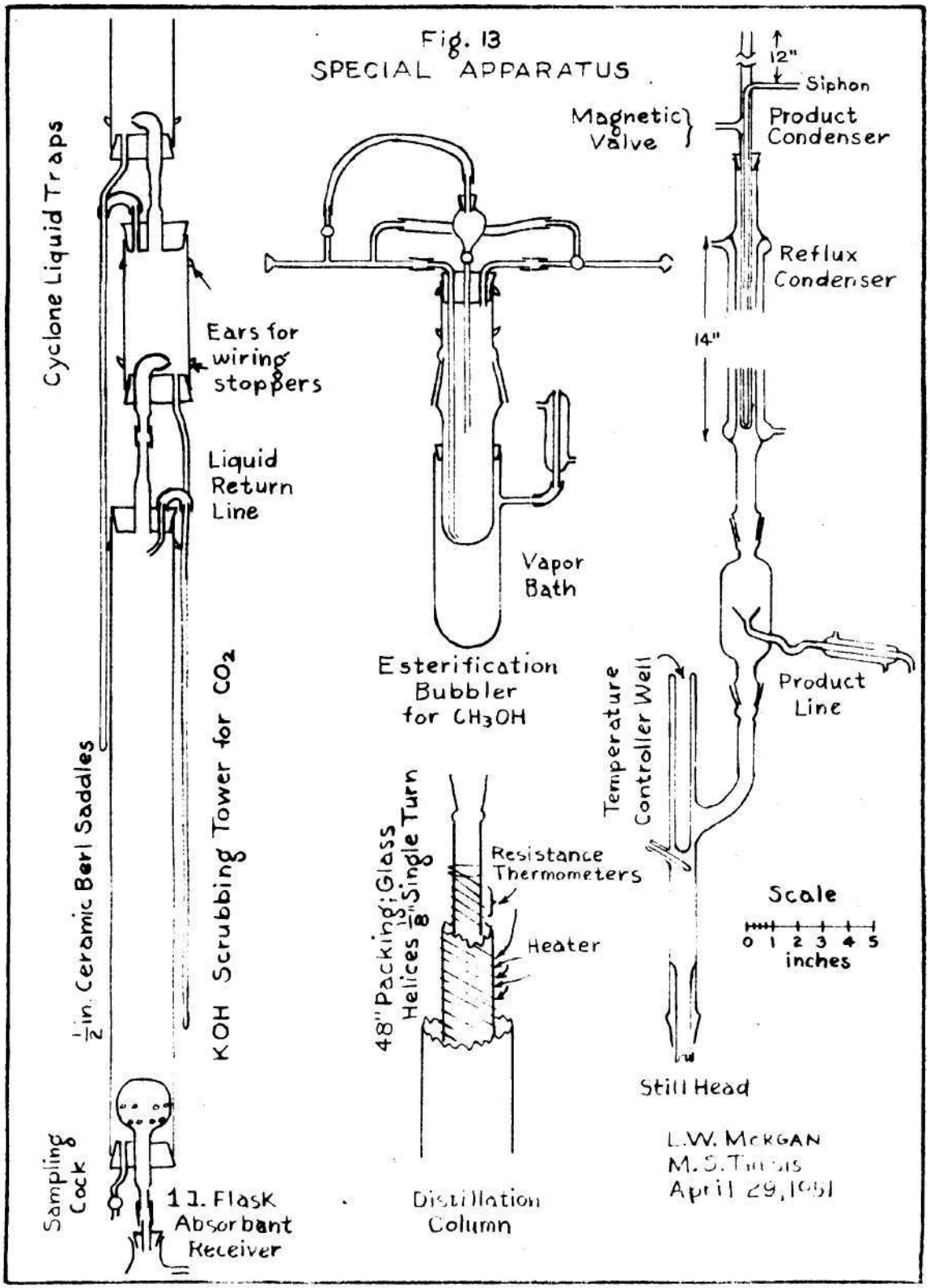
April 29, 1951

Fig. 13
SPECIAL APPARATUS



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